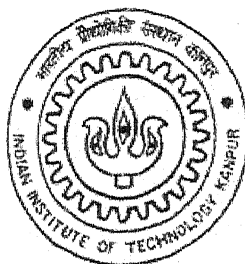


**Micellar Enhanced Ultrafiltration
in CSTR Mode cell:
Optimization of operating conditions**

*A thesis submitted
in partial fulfillment of the requirements
for the degree of
Master of Technology*

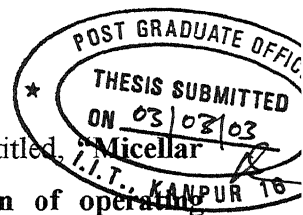
**By
S.Sujatha**



to the
DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

February, 2003

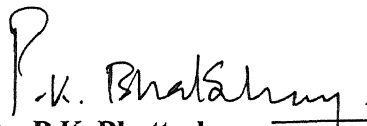
CERTIFICATE



This is to certify that this is a bonafied record of thesis work entitled, **Enhanced Ultrafiltration in CSTR Mode cell: Optimization of operating conditions**, by **S.Sujatha** in partial fulfillment of the requirements for the degree of **Master of Technology** in Chemical Engineering of Indian Institute of Technology, Kanpur. It has been carried out under my supervision and this work has not been submitted elsewhere for a Degree.

28th February, 2003

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Dedicated to.....

Parents & Sisters

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ABSTRACT

Ultrafiltration experiments were carried out with SDS (anionic) and Triton X-100 (non-ionic) surfactant mixture in 7:3 ratio, respectively, in continuous stirred tank reactor (CSTR) mode (designed and fabricated) and in batch mode UF cells, in order to study retention characteristics of surfactants mixture, using 5000 MWCO neutral membrane. Influence of independent operating conditions, like pressure and total feed concentration on the permeate flux and retention of surfactant were observed. It was observed that there was no effect of concentration polarization on flux in CSTR mode, as flux remained constant with time and showed linear variation with pressure. Further, percent retentions and flux were found to be higher in case of CSTR mode compared to batch mode. Increase in total surfactants concentration showed increase in percent retention and decrease in flux; but, percent retention decreased with increase in applied pressure gradient. This may be because of breakage of micelles during continuous operation.

The work was carried out with the aim of removing metal ion (present case: Cu^{++} , in the form of copper sulphate), using above stated mixed surfactants, during micellar enhanced ultrafiltration (MEUF) operation under optimized conditions of process variables; as the removal characteristics of metal ion strongly depends upon retention characteristics of mixed surfactant (largely present) during MEUF operation. Therefore, the process variables were optimized with respect to retention characteristics of mixed surfactants.

Experimental values (exclusive surfactants based UF results) of flux and retention as functions of applied pressure and total feed concentration were utilized, in the form of developed empirical equations, and then optimization was carried out using NSGA-II. Exclusive copper ion solution runs showed a maximum 7 percent retention. This retention was considered due to adsorption of copper ions with the polymeric membrane surface. Optimized operating conditions (*Total feed concentration: 41.5 mM; and Pressure: 758 kPa* → *Optimized variables*) with respect to SDS and Triton X-100 runs were utilized for the separation of copper during MEUF operation. Very high values (more than 99.84%) of retentions of copper were achieved under optimized conditions of UF process variables.

Nomenclature

a	molar extinction coefficient ($\text{mole}^{-1}\text{l}^{-1}$)
A	membrane area (m^2), absorbance
C	concentration (mole/l)
C*	CMC of surfactant mixture
f	activity coefficient
G	free energy (J/mole)
H	enthalpy (J/mole)
J	permeate flux (m/s)
K	mass transfer coefficient
L	cell path length
M	molecular weight (g/mole), micelles
N	aggregation number
P	pressure (kPa)
R	gas constant (J/mole-K), resistance (m), retention
S	entropy (J/mole-K)
t	time(s)
T	absolute temperature (K)
V	volume (m^3)

Greek letters

Δ	difference
λ	wavelength (nm)
μ	viscosity (Pa-s)
ν	kinematic viscosity (m ² /s)
π	osmotic pressure (kPa)
ρ	density (kg/m ³)
α	mole fraction

Subscripts

b	bulk
c	copper
eq	equilibrium
f	feed, fouling
j	component
m	membrane
ma	mass action
M	micellar phase
o	observed, initial
p	permeate
ps	phase separation
r	real
s	surfactant
total	total mixed surfactant
w	water

Superscripts

0

standard state

Abbreviations

Amp	ampere
CMC	critical micellar concentration
CPC	cetyl pyridinium chloride
CSTR	continuous stirred tank reactor
CTABr	cetyl trimethyl ammonium bromide
conc.	concentration
Hz.	Hertz
MAL	micellar aggregation layer
MEUF	micellar enhanced ultrafiltration
MOOP	multi-objective optimization problem
MWCO	molecular weight cut-off
NSGA	non dominated sorting algorithm
SDS	sodium dodecyl sulphate
soln.	Solution
TX	Triton X-100

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Micellar enhanced ultrafiltration, or MEUF, is proving to be effective in removing solutes, which have lesser retention through the process of ordinary ultrafiltration. In this process, surfactant (MW ~ 250 to 800) is added to the effluent stream at concentration greater than the critical micelles concentration (CMC) so that they form aggregates of about 50-150 molecules, called micelles. Hydrophobic organic pollutants or metals ions, present in the aqueous suspension of micelles, tend to either solubilize in the interior or adsorb on the surface of the micelles [1]. If the tendency for metal ion to be attracted on the micelle is strong, a large fraction of metal ions or dissolved organic molecules are thus 'trapped' (may be called as) by micelles. Micelles, along with bound ions or pollutants, by virtue of being much bigger in size (MW – 20,000 to 150,000; depending upon type and concentration of surfactants) than the chosen MW cut-off size of the membrane (much less than micelle size) for ultrafiltration, get retained by such a membrane. The permeated stream contains low concentration of unattached metal ions or unsolubilized organic solutes and surfactant monomers. A schematic sketch of MEUF is shown in Fig.1.1. The process is versatile enough to include the separation of hydrocarbons, removal and recovery of organic acids and amines, apart from the several other separation and concentration of metal ions. Most of the research studies on MEUF were carried out in a batch UF cell, using either stirred or unstirred mode, to understand the retention behavior of micelles along with bound ions or solutes [2, 3, 4, 5]. However, practically no information is available on the application of MEUF under continuous mode. Therefore, an attempt has been made to study the retention behaviour of micelles in a continuous mode, which may facilitate understanding of the potential of MEUF operation in terms of its application for the removal of a metal ion.

Theoretically, the metal ion concentration in the permeated stream should be equal to (practically at times may be less) the concentration of the unbound ions in the

retentate. Similarly, the surfactant concentration in the permeated stream may be found to be equal to or less than the surfactant monomer concentration in the retentate. As either of these two concentrations is low, the permeated stream thus obtained is of high purity. The retentate stream can then be treated for the recovery of metal ion and the surfactant.

Suitability of surfactant is decided on the basis of the extent of solubilization of organic solute or adsorption of metallic ions on the surface of the micelles. It has been observed that the surfactant having charge opposite to that of the target ions has higher efficiency in entrapping the solute or metal ions. The binding of hydrophobic solutes to both ionic and nonionic solutes were considered and was shown to be a function of the molecular structure of the surfactants, the concentration of the surfactant and the electrolytic composition of water [6].

The retention characteristics of the membrane are of utmost importance while studying MEUF phenomena for the removal of metal ion. Therefore, operating conditions (like applied pressure gradient, feed surfactant concentration and feed flow conditions) play a vital role in dictating retention characteristics through MEUF operation. It would be, therefore, interesting to study in detail the influence of operating conditions on retention characteristics through MEUF, using only surfactant solution (with concentration below and above CMC) without the presence of metal ion. Such an attempt may enhance the understanding of surfactant solution behaviour during MEUF. Further, an attempt of optimization of operating conditions with respect to retention characteristics may prove to be the most suitable conditions for the removal of metal ion through MEUF. In such an attempt, the present work undertakes the removal of copper ion under optimized operating conditions of MEUF operation in a continuous mode.

Copper is a heavy metal that is toxic in unbound form. Wastewater discharged by industrial activities is often contaminated by a variety of toxic or otherwise harmful substances. Increasing concern about the impact of industrial activity on the

environment leads to more stringent control of water and effluent discharge. Metal containing wastewater arise from a variety of sources, such as metal plating circuit board manufacturing, photographic and photo processing, refineries and metal finishing industries, etc. Generally, most of the metal ion pollutants are non-biodegradable and quite a few of them are highly toxic and have carcinogenic effect. Removal of such toxic organic materials and heavy metals, although present in small quantities in aqueous solutions, pose challenging problems to scientists and engineers. Conventionally, the processes and technologies involved in the removal of heavy metals from industrial wastewater are precipitation, ion exchange, complexation, adsorption, evaporation and electrochemical processes. However, the use of these processes is limited due to number of constraints, such as over use of materials and high operating cost. Even after rigorous treatment, often these processes cannot achieve the standards for open water or sewer discharge (Standard concentration of Cu^{++} is limited to 1.3 ppm for disposal to open water has been set by world health organization, WHO).

There have been some attempts to minimize the excess use of surfactants during MEUF [7]. This objective was met by combining ionic with non-ionic surfactants which essentially reduce the concentration for the formation of micelles; obviously the CMC [8]. Most of the studies, carried out earlier, were pertaining to MEUF systems using a batch cell (stirred or unstirred) and were based on the use of single surfactant (ionic or non-ionic). Little information is available on the application of mixed surfactants, particularly with regard to removal of metal ions and organic solutes. Therefore, an attempt is made to study MEUF operation with mixture of surfactants; especially with regard to surfactant being the key compound. The approach is in the direction of utilizing special properties of surfactant mixtures in order to operate MEUF, efficiently and economically. As stated earlier, the important feature of a mixed ionic and nonionic surfactant system is its significantly lower CMC in comparison to CMC of single surfactant.

Few studies, carried out earlier, are to remove and recovery of copper from an aqueous solution through MEUF. Ligand modified MEUF operation, in comparative with solvent extraction, was used for removal of copper, and observed to have incurred higher capital and operating cost. In the past, researchers have attempted to use mixed surfactant system for removal of Cu^{++} from aqueous solution.

The present work has been under taken to study the characteristics of MEUF operation using a continuous (continuous stirred tank reactor cell) UF cell and anionic and nonionic surfactant mixture (SDS-anionic and Triton X-100-nonionic; in the ratio of 7:3) along with Cu^{++} in the form of copper sulphate in aqueous solution.

With above introduced background and importance of topic, the broad objectives of the present work are:

- 1) To study the influence of operating conditions (concentration of total surfactant solution and applied pressure) on the permeate flux and the retention of surfactants.
- 2) Optimization of operating conditions (applied pressure and total surfactant concentration) using NSGA-II technique.
- 3) To observe the amount of copper retention under optimized conditions.

Micellar Enhanced Ultrafiltration

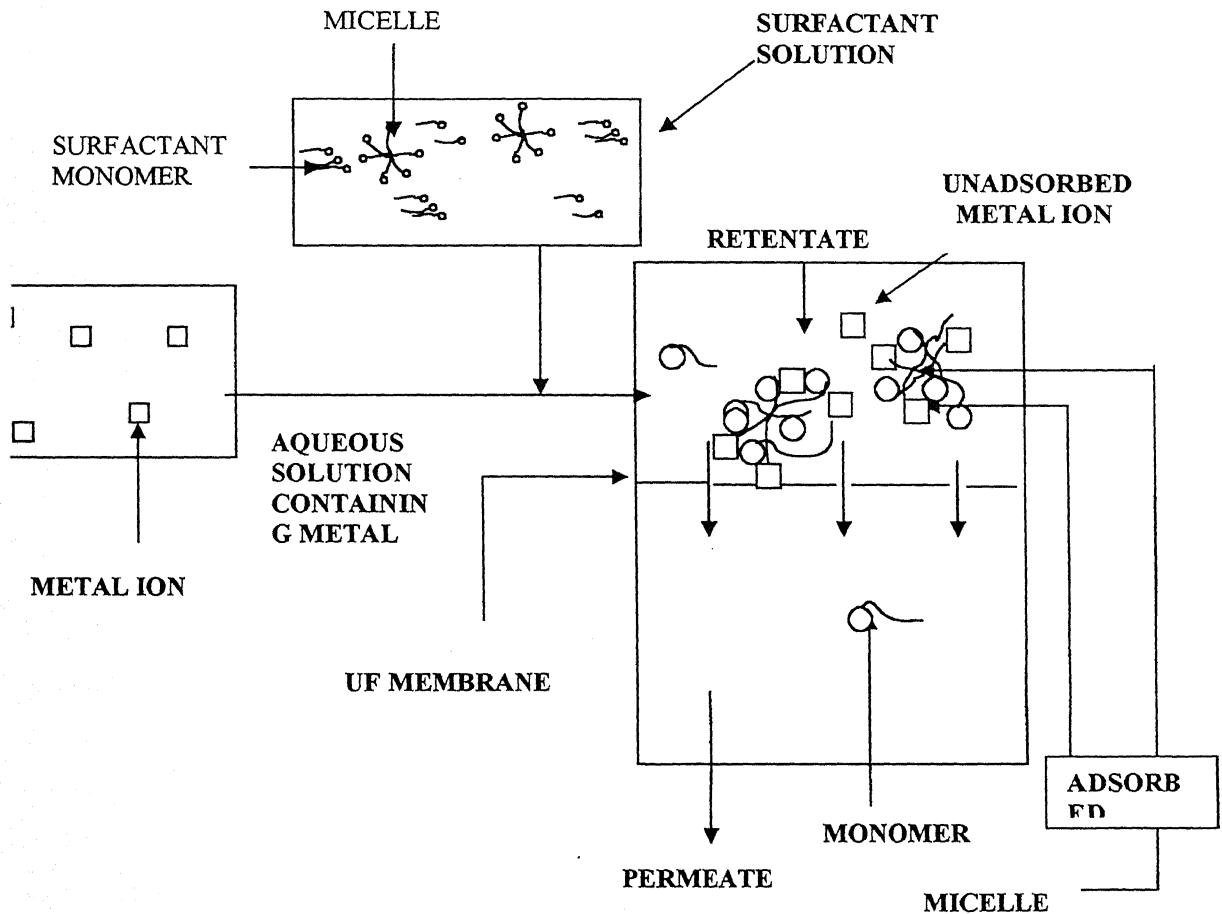


Fig. 1.1 Schematic of Micellar Enhanced Ultrafiltration to remove dissolved metal ions from water

2.1 Separation Processes for the Removal of Metal Ions from Aqueous Stream

The presence of heavy metals in waste and surface water is becoming a severe environmental and public health problem. Some of the common processes employed for removal of these ions from wastewater streams are electrolytic method, ion exchange method, activated carbon adsorption, cellulose xanthate process, solvent extraction, coagulation, chemical precipitation, etc. However, the conventional treatment methods like hydroxide precipitation, electrolytic method, sulphide precipitation, have limitations with regard to stringent pollution norms. These are generation of sludge, loss of expensive chemicals to wastewater, cost of treatment chemicals, etc. Among these, sludge generation and disposal is the most pressing problem.

Ion Exchange Process

Ion exchange is a reversible chemical reaction wherein an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. The synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications.

Following is the selectivity sequence of an anion exchange resin:

citrate>sulphate>oxalate>iodide>nitrate>chromate>bromate>SCN>chloride>formate>acetate>fluoride>hydroxide.

Even though, ion exchange is suitable for treatment or materials recovery from very dilute solutions, the process is expensive as ion exchange resins and regenerating chemicals are costly, in addition this process is inapplicable to wide pH range.

Activated Carbon Adsorption

Activated Carbon Adsorption is an emerging technology for removal of inorganic species from wastewater such as cyanides, heavy metal ions, etc. Adsorption is defined as the collection of a substance onto the surface of adsorbent solids. It is the removal process

where certain particles are bound to an adsorbent particle surface by either chemical or physical attraction. The activated carbon is an effective adsorbent material due to its large number of cavernous pores, which provide a large surface area. However, the maximum adsorption capacity of carbon is much pH sensitive and decreases rapidly with the change in pH.

Activated carbon is expensive and need to be regenerated. The regeneration and disposal of carbon containing metal ions is by itself a problem. Moreover, this process fails to produce an effluent with metal ion concentration at per with wastewater disposal norms, especially if the concentration of metal ions in the feed is high.

Modified Activated Carbon Adsorption

Modified activated carbon are carbonaceous adsorbents which have tetrabutyl ammonium iodide (TBAI) and sodium diethyl dithiocarbamate (SDDC) immobilized at their surface. This modified adsorbent used for the adsorption of toxic ions, copper, chromium, zinc and cyanides in wastewater. This modified technique enhances the removal capacity of carbon and therefore decreases cost-effective removal of Cu(II), Zn(II), Cr(II) and CN^- from wastewater. The TBA-carbon modification has a cyanide removal capacity of approximately five times to that of plain carbon. The SDDC-carbon showed Cu, Zn, Cr removal capacity from two to four times higher to that of plain carbon. The removal of these metal ions follow a descending order pattern [9], $\text{Cu} > \text{Zn} > \text{Cr}$.

In this also regeneration and disposal of carbon, containing metal ions, is problem.

2.1.1 Other Separation Processes for the Removal of Copper:

Removal of silver and copper by supported liquid membrane

Facilitated counter-transport of silver and copper ions, both in acidic thiourea medium, across a supported liquid membrane (SLM) by using di(2-ethylhexyl)phosphoric acid (D2EHPA) as a carrier, dissolved in chloroform. The parameters, influencing the transport of silver and copper are: thiourea concentration in the feed phase, pH of feed solution, temperature of the system, membrane support characteristics and the type of acid [10]. Thiourea can form with both ions complexes, which becomes less mobile than the free metal cations.

Copper removal from water by ligand-modified micellar-enhanced ultrafiltration.

In ligand-modified micellar-enhanced ultrafiltration (LM-MEUF), a surfactant and a ligand are added to an aqueous solution containing ions of like charges. Most of turn to micelles if the concentration is well above its critical micelle concentration (CMC). The hydrocarbon chains of the surfactant occupy the micelle interior, making this core hydrophobic; hydrophilic portions of the surfactant situate at the micelle surface. A suitable ligand for LM-MEUF has both the moiety needed to complex the target metal ion. Large hydrophobic groups are responsible for solubilization of target ions into the micellar hydrophobic interior. Once the ligand selectively complexes with the target ions, the metal-ligand complex will also become associated with the micelles and thus get retained by UF membrane of MWCO size much less than the ligand size. The comparative economic analysis indicates a 17% higher capital and a 43% higher operating cost for LM-MEUF process compared to the solvent extraction process [11].

Biological Removal of Copper from Industrial Wastewater

The removal of Copper and other heavy metals, in low concentrations, from industrial wastewater was studied using different biosorption systems: a) bacterial biofilm supported by activated carbon, b) breweries residual yeast biomass and c) purified alginate.

Above citations are some of the conventional processes with their associated disadvantages. With rising costs and stricter environmental norms, newer processes are being explored for the removal of metal ions. This paved the way for the emergence of membrane based separation process as an alternative to traditional separation processes. Membrane technology appears promising owing to low capital cost, low space requirement, low labour costs, low energy requirements, and negligible sludge.

The membrane processes, which are significantly useful for the purpose, are described below with their importance:

An emerging application of Microfiltration (MF) is in the treatment of wastewater, particularly municipal sewage. When operated in conjunction with high-speed

bioreactors, very low overall retention times with excellent removal of particulates including bacteria and viruses, is reported in pilot trials [12].

One of the important applications of electrodialysis [ED] in wastewater treatment systems is to process rinse waters from electroplating industries. ED has successfully treated dump leach water containing heavy metals. The regeneration of chemical copper plating bath has been studied in a pilot plant stage [13]. ED, as compared to reverse osmosis (RO), can use more thermally and chemically stable membranes and hence the process can run at elevated temperature with solutions of high and low pH. However, in this perspective the ED has a disadvantage; that it can remove only the ionic components. Municipal water supplies are frequently of inadequate quality for industrial and commercial processes. RO is now widely used to upgrade these water supplies. The most important single application is the electronic industry, where high quality rinse water is essential. RO can be used for pollution control. Some specific applications include treatment of electroplating rinse waters to recover metals; in which the treated water is suitable for reuse.

To summarize the applications of membrane processes like RO, UF, MF and ED, it may be observed that all these processes essentially remove solutes from micro to macro levels with the exception of ED where ionic solutes are separated. Practically there are no available informations, which describe the applications of these processes towards separation of metals in ionic form. Application of ED, particularly for hexavalent chromium separation, also does not find any mention in the literature. However, there are reports of use of integrated membrane processes, which may tackle the problem of metal ion separation. One such emerging process is micellar-enhanced ultrafiltration.

2.2 Micellar Enhanced Ultrafiltration (MEUF)

Micellar enhanced ultrafiltration can be used to remove dissolved multivalent ions from water [14]. An appropriate concentration of surfactant of opposite charge to that of the ions is added to the aqueous stream, so that a large fraction of the surfactant exists in the micellar form. The target ions get bound or adsorbed on the micelles due to electrostatic attraction. When the resulting solution is passed through an ultrafilter having pore diameters smaller than micelle diameter, most of the surfactant with bound metal ions in

micelles remain in the retentate solution. The permeate solution passing through the membrane is, in many cases, practically pure water [14]. This process can also be used for the separation of hydrocarbons and removal and recovery of organic acids, alcohols, and amines [15].

2.2.1 Removal and Recovery of Organic Solutes

MEUF results for the removal of 4 tert-butyl- phenol (TBP) using CPC as surfactant were reported for membranes with pore sizes ranging from 1000 to 50,000 MWCO [16]. The removal of n-alcohols and cresols by MEUF, using CPC as the surfactant was also reported [17]. The effect of retentate CPC concentration on permeate flux and permeate CPC concentration was studied [1]. Experimental work on micellar enhanced ultrafiltration of CPC solution in batch cell at constant flux was also carried out [2].

Separation of phenol and 4- nitrophenol by means of hexadecyltrimethylammonium bromide (CTAB), sodium dodecyl sulphate (SDS), alkyl polyglucoside (APG) and oxyethylated methyl dodecanoate (OMD) from water and NaHCO_3 solution was reported [18]. The approach has been made to evaluate the resistance of secondary layer and its change as a function of flux, time and the effect of pollutants and modifiers.

MEUF was applied to mixtures containing phenol or O-cresol and simultaneously, Zn^{2+} and / or Ni^{2+} , using an anionic surfactant [18]. The results demonstrated that removal of organic solute was not significantly affected by the presence of metal ions and vice - versa. This is because, the predominant mechanism of removal of metal ions were totally different. The ability of MEUF to simultaneously remove organic and multivalent metal ionic solutes makes it economically attractive.

The effect of important operating parameters (applied pressure, concentration of solutes and surfactants) on the extent of separation of organic solutes (aniline and phenol) was observed [20]. Solubilisation of these solutes in CPC micelles was experimentally ascertained. Solubilisation equilibrium constant of phenols in CPC was estimated to be around four times to that of aniline. A mathematical model developed in this study [15] was used to describe the separation of organic solutes by MEUF and predict permeate solute concentration under varying operating conditions. Equilibrium distribution constants of phenol between surfactant micelles and water were determined by MEUF

using commercial ultrafiltering centrifuge tubes [21]. Three surfactants: sodium dodecyl sulphate (SDS), polyethylene 20 cetyl ether (C16E20) and cetylpyridium chloride (CPC) were tested with a 10,000 MWCO membrane.

A steady state combined resistance in series and osmotic pressure model was proposed [3] to predict the flux in laminar, cross flow ultrafiltration of micellar CPC solution. The data were obtained from a study of CPC monomer – micellar equilibrium in aqueous solutions using UF [22].

1.2.2 Separation and Concentration of Metal Ions

The application of MEUF for removing heavy metal ions from water is getting noticed. MEUF was found to be extremely effective in separating Cu^{2+} and a rejection of 99.8% was observed using single surfactant when present in dilute concentration [23]. However, the permeate purity decreased as the metal concentration in the feed increased. Further, purity also gets affected by the reduction in surfactant concentration and or with the presence of monovalent salt in the solution.

MEUF of gold (III) from hydrochloric acid media was also studied [24] using polyoxyethylene nonylphenyl ethers (PONPES) as a nonionic surfactant. The rejection efficiency of gold (III) increased with increasing surfactant concentration, ethylene oxide number of PONPE and the applied pressure as well as decreasing molecular weight cut-off of the membrane. It was found that the use of MEUF with PONPE provides higher selectivity to gold (III) than those with charged surfactant such as cetyl pyridinium chloride (CPC) and sodium dodecyl sulphate (SDS).

Traces of aluminum were preconcentrated [25] in water by forming a complex with lumogallion. Thereafter, it was successfully accumulated in the micellar phase, obtained from cationic and non-ionic surfactants, and filtered through 10,000 MWCO ultrafiltration membranes. It was reported that at pH 5.9, with 1×10^{-3} M lumogallion and 2×10^{-2} M cetyltrimethylammonium bromide, quantitative retention of aluminum present at $\mu\text{g/ml}$ concentration level was achieved.

Lecithin, a natural, nontoxic, and biodegradable surfactant exhibits emulsifying characteristics, which may be used for MEUF. The binding of various lecithins to cadmium, copper, lead, nickel and zinc in a mixture as well as individually were

observed [26]. In the presence of all five heavy metals, the lecithin showed the highest affinity for Cu than for Cd and Zn whereas Ni was found to have the lowest affinity. The affinity for Cd and Zn were found to be similar. In experiment when only one metal was present, lecithin exhibited the following affinity: Ni>Cu and Zn>Cd; whereas Cu and Zn showed similar affinity. Lead was not bound significantly in the either scenario.

Industrial wastewater from metal plating, petroleum refining, chemical and food processing plants vary in composition and may contain toxic substances like heavy metal cations and chemical compounds in the aqueous phase and oil fractions. It had been proposed [27] to combine MEUF and algae containing membrane bioreactors (MB) to completely remove the metal ions from metal finishing industry's effluent. MEUF, with lecithin as surfactant, was found to remove heavy metals from aqueous (50 – 90% removal) and non-aqueous wastes (90 -97% removal). Continuous binding and separation of ions through membrane bioreactors that were 20 -50 times more efficient than conventional bioreactors, increased the efficiency of removal of trace levels of heavy metals.

The removal of hexavalent chromium by micellar enhanced ultrafiltration using cetyl trimethylammonium bromide (CTABr) as well as cetyl pyridinium chloride (CPC) was experienced [4]. Effect of metal ion concentration, surfactant concentration, presence of monovalent salt against varied transmembrane pressure drop, feed velocity and temperature were studied. Rejection coefficients, higher than 99%, were obtained as long as the feed concentration is less than or equal to 200 times the standard. The rejection rate was found to depend on ionic strength and pH. The increase of ionic strength decreased the retention of chromate ions and permeate surfactant concentration. As long as the NaCl feed concentration was less than or equal to 100mM, more than 88% of hexavalent chromium were retained and surfactant leakage was reduced [4].

Addition of small concentration of nonionic surfactant to anionic surfactant results in anionic nonionic mixed micelles and exhibit negative deviation from ideality of mixing. This leads to smaller fraction of surfactant being present as monomer and subsequently a large fraction present in micellar form [23]. It was reported that addition of nonionic surfactant improved the separation of Zn^{2+} substantially at total concentration above CMC of anionic surfactant. Both Zn^{2+} and tert – butylphenol showed unexpected

ejection at surfactant concentrations moderately below the CMC. This was considered to be due to a higher surfactant in the gel layer, adjacent to the membrane where micelles were present.

A lab study was conducted to evaluate the effects of composition and concentration of mixed anionic / nonionic surfactants on the study of MEUF operation for the removal of metal ions / organic solutes from aqueous solution [7]. Based on the analysis of surface tensions and micelle sizes, it was found that for mixed sodium dodecyl sulphate (SDS) / Triton X-100 surfactants, mixed micelles were formed for which the CMC was significantly lower than that of SDS alone. The rejection of Cu^{2+} was found to be negligible with a surfactant concentration 10mM, on using pure Triton X-100. Whereas the rejection increased upto 85% on increasing the SDS mole fraction, indicating the mechanism of Cu^{2+} rejection being chiefly due to the electrostatic attraction. When MEUF technique was applied to Cu^{2+} and phenol simultaneously from aqueous solution, Cu^{2+} rejection was slightly enhanced in the presence of phenol [7]. However, rejection of phenol was comparatively low approx. 27% [11].

2.3 Miscellaneous Applications of MEUF

Micellar Enhanced Ultrafiltration was used to recover thuringiensin from the supernatant of *Bacillus thuringiensis* fermentation broth using CPC [28]. On manipulating various possible process variables, it was found that CPC concentration and membrane pore size were the two major factors to the increase recovery of thuringiensin. It was also reported that ionic strength, pH adjustments were not necessary and micelle formation temperature was not important within the temperature range studied. The bioassay results showed that the spray- dried thuringiensin with CPC was more toxic to fly larvae than without CPC. This indicates that CPC not only facilitated thuringiensin recovery but also improved the insecticidal effect.

2.3 Structure of Surfactants

Surfactant is a diminutive term for SURFace ACTive AgeNT. Surfactants are materials that tend to not only accumulate at the surfaces or aggregate in solutions, but by their presence, they also change the properties of surfaces and solutions. More generally, they

are active at the interfaces. Surfactant molecules have two distinct parts, one that has an affinity to the solvent (hydrophilic in case of aqueous solution) and the other that does not have any affinity (hydrophobic). It is the tendency of the hydrophobic part of the molecule to aggregate because of their mutual dislike for solvent. This dislike tends to become the driving force for the surfactant self – association. The hydrophilic head groups remain spaced out in the solution.

The properties of surfactants fall into two broad categories: adsorption and self – assembly.

Adsorption is the tendency for a surfactant molecule to collect at the interface. This molecular property leads to the macroscopic properties of wetting, foaming, and emulsion formation.

Self – assembly is the tendency for the surfactant molecules to organize themselves into extended structures in water. This includes the formation of micelles, bilayers and liquid crystals.

Surfactant can be broadly classified into ionic, nonionic and zwitter ionic classes. Ionic can be both anionic and cationic surfactants [29].

Anionic Surfactant

This type of surfactant on dissociation in a liquid form results in a negatively charged ion. Commonly used anionic surfactants are alkyl sulfates, alkyl benzenesulfonates, alkyl sulfonates and the alkyl phosphates. In fact, probably the most studied surfactant over the years is one of the alkyl sulphates: sodium dodecyl sulphate.

Anionic surfactants are widely used .They are used in shampoos, in dishwashing detergents and in washing powders. In many industrial and commercial applications, they are used in conjunction with nonionic surfactants to provide even greater stability.

Cationic Surfactant

This type of surfactant on dissociation in a liquid form results in positively charged ion. Alkyl pyridinium and quaternary ammonium salts provide excellent surfactants that can be used over a range of conditions. Cetyl pyridinium chloride and cetyl trimethyl ammonium bromide are the most commonly used cationic surfactants. They are used in things like hair conditioner and fabric softeners. The fatty amine salts are quite useful along with nonionic surfactants, giving good stability over a range of pH levels [29].

Amphoteric or Zwitterionic Surfactant

This type of surfactant contains both positive (cationic) and negative (anionic) groups. In acidic solutions they form cations and in alkaline solutions they form anions. Whereas, in the middle range of pH they become molecules with two ionic groups of opposite charges known as Zwitter ions. The key property of amphoteric surfactants is the compatibility with aqueous ions and being resistant to both acids and alkalis. Therefore, they are often used for foaming, wetting and emulsification in personal care products [30].

Non-ionic Surfactant

This type of surfactant on dissociation in liquid form does not result in either positively charged or negatively charged ions. They are referred chiefly to polyoxyethylene or polyoxypropylene derivatives. However, other surfactants are also included such as, fatty monoamides and amine oxides. They are usually prepared by addition of ethylene oxide to alkyl phenols, fatty acids and alcohols, fatty mercaptans and amines.

Another class of nonionic surfactants is alkyl polyglycosides. At least, for the last 20 years, these have been dubbed the “new generation nonionic surfactants”. In these molecules, the hydrophilic group is sugar. Alkyl glycoside and glucose ester are examples of alkyl polyglycosides.

Nonionic surfactants differ from both cationic and anionic surfactants in that the molecules are actually uncharged. The hydrophilic group is made up of some other very water-soluble moiety, (e.g. a short, water-soluble polymer chain) rather than a charged species. Traditionally, nonionic surfactants have used polyethylene oxide chains as the hydrophilic group [31].

The predominant use of these surfactants is in food and beverages.

Nonionics do not contain ions and hence solubilise over the pH range. Their solubility is due to hydrogen bonding between the hydrophile and water molecules. Amphoterics have both anionic and cationic groups, so they are soluble in water over wide pH limits; even wider than nonionics. Whereas, nonionics lose their solubility at low and high pH, and at high electrolyte levels, as electrolytes compete with ethoxylate chain for hydrogen bonded water.

2.4 Micelles : Structures and Properties

When surfactant molecules are present in aqueous solution at concentrations above their critical micellar concentration (CMC), interactions between the hydrophobic alkyl chains of adjacent molecules provide a force tending to pack them closer to each other. The hydrophilic head groups, on the other hand, have a strong affinity for water and tend to remain spaced out in the aqueous medium. When the head groups are charged, electrostatic repulsion provides additional force tending to distance the head groups. These opposite forces govern the formation and growth of micelles. The micelles continue to grow until the energy released from the condensation of alkyl chains is balanced by the work done to bring the hydrophilic head groups (which may be charged) into the micellar surface.

The existence of different shapes and sizes of micelles are described [16]. They are also interchangeable from one form to another. These are spherical, cylindrical, flexible-bilayer, planar-bilayer and inverted micelles, depending upon the conditions prevailing in the system. Micelles are not fixed entities but have a transient character. Surfactant molecules rapidly join and leave the micelles, whose aggregation number presents only an average over time.

Stigter [11] introduced a detailed model for ionic micelles. According to this model, the small micelle consists of a spherical hydrocarbon core and an aqueous *Stern layer*. The radius of the micelle is equal to the length of the alkyl tail of the surfactant. The *Stern layer* consists of hydrophilic heads of the surfactant molecules along with a fraction of the counter ions. Outside of the Stern surface is the Gouy – Chapman diffuse double layer, which contains an excess of counter ions equal to the charge of the micelle. Model for SDS is shown in Fig.2.2

2.5 Selection of Surfactant

In the selection of surfactant for use in MEUF, some important desirable characteristics are [16]:

- [1] high solubilisation capacity for the organic pollutant or adsorption capacity for metal ions

[2] forms large micelles, so that large pore sizes can be used and

[3] low monomer concentration, so that little surfactant is wasted

One desirable characteristic of a surfactant is a long hydrocarbon chain as this result in the formation of larger micelles with high solubilization capacity and low monomer concentration. Nonionic surfactants form large micelles and have low monomer concentrations in micellar solutions. However, the solubilisation or adsorption capacities of the nonionic surfactants are not high compared to anionic or cationic surfactants. Copper exist in the form of Cu^{+2} in aqueous solution, so the opposite charged anionic surfactants are used in the recovery of copper in MEUF.

2.6 Recovery of Surfactant

It is important to recover surfactant for reuse in to make the process economical. The recovered surfactant will normally be recycled to the process to minimize makeup surfactant requirements.

The process functions on the basis of precipitation of surfactant by using monovalent or multivalent counterions. The surfactant is precipitated from the aqueous solution by addition of an ion of opposite charge to that of surfactant (the counterion). The precipitate is removed from solution by gravity settling, filtering, or centrifuging. This filter cake is then recycled or further treated if the counterion used for the precipitation is unacceptable in the process. Ultimate recoveries of 95% were shown to be attainable using this process [16].

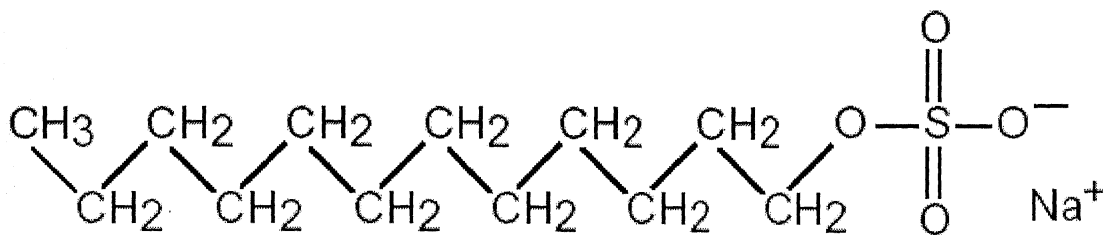


Fig.2.1a Molecular structure of Sodium Dodecyl Sulphate (SDS)

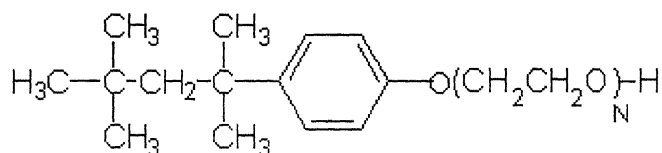


Fig.2.1b Molecular structure of Triton X-100, N = 10

Fig.2.1 Molecular structure of surfactants

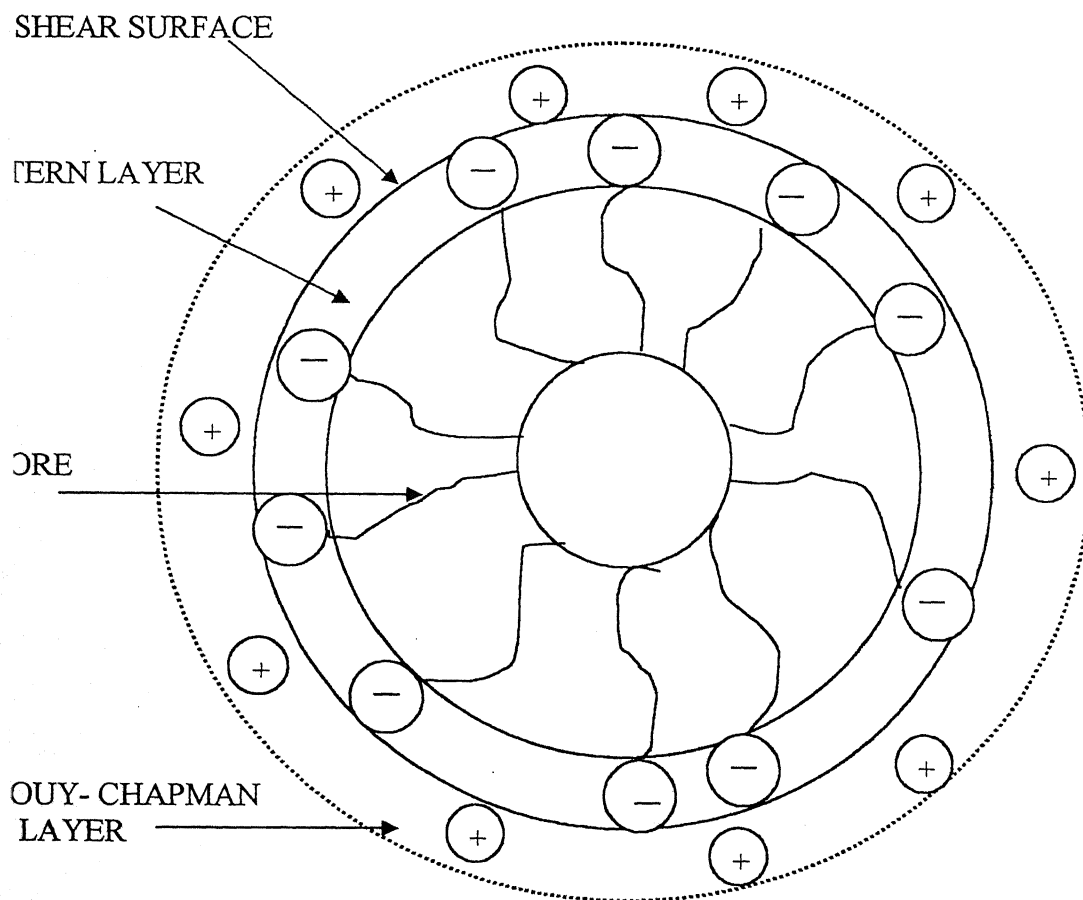


Fig.2.2 Structure of Sodium dodecyl sulphate (SDS) micelle

3.1 Micelle

When surfactants are added to aqueous streams above CMC, they form aggregates of about 50-150 molecules, called micelles. Micelles exist in different shapes and sizes. They are interchangeable from one form to another. Micelles are not fixed entities, but are dynamic in nature. The surfactant molecules rapidly join and leave the micelles, whose aggregation number is only an average over the time.

As described earlier micelle consists of a spherical hydrocarbon core and aqueous Stern layer. A probable structure of micelle is given in the Fig. 2.2. The radius of micelle is approximately equal to the length of the alkyl tail of the surfactant.

3.1.1 Aggregation Number

The number of monomeric surfactant molecules contained in a micelle provides aggregation number. It can be obtained by dividing micellar molecular weight by monomeric molecular weight. Molecular weight of the micelles can be obtained from various techniques including gel filtration, light scattering, sedimentation equilibrium, and small angle X-ray scattering. Aggregation number is influenced by the ionic strength.

$$\frac{\text{micellar molecular weight}}{\text{monomeric molecular weight}} = \text{Aggregation number} \quad (3.1)$$

3.1.2 Concentration of Micelle

CMC may be defined as the lowest concentration above which the monomers cluster together to form micelles. Given CMC, concentration of surfactant and the aggregation number, it is possible to calculate the concentration of micelles in moles/liter using the following equation:

$$\text{Concentration of [micelles]} = \left(\frac{C_0 - \text{CMC}}{N} \right) \quad (3.2)$$

where, N is the aggregation number

C_0 is surfactant concentration

3.1.3 Thermodynamics of Micelle Formation

Two general approaches deal with the micellization. In the first, micellization is regarded as a phase separation, which commences at CMC. CMC is taken to represent the saturation concentration for unaggregated surfactant. In the second approach, micelles and single surfactant ions are considered to be in association – dissociation equilibrium. The CMC in this approach is merely a concentration range above which most of the surfactant appears in micellar form.

Phase Separation Approach

The equilibrium between surfactant ions D^+ , counterions X^- and micelles M is as follows:



The micelle charged aggregate of surfactant ions plus an equivalent of counterions in the surrounding region are treated as a separate phase. The standard free energy of micellization per mole of monomer is given by [29]:

$$\Delta G_{ps}^0 = \frac{-RT}{j} \ln \left(\frac{f_M [M]}{f_D^j f_X^j [D^+]^j [X^-]^j} \right) \quad (3.4)$$

where $[M]$, $[D^+]$ and $[X^-]$ are equilibrium concentrations and f_M , f_D and f_X are the respective activity coefficients.

The standard heat of micellization is [30]:

$$\Delta H_{ps}^0 = -RT^2 \frac{d}{dT} \left[\ln (f_D f_X [CMC] [X^-]) \right] \quad (3.5)$$

The standard enthalpy of micellization is given by [29]

$$\Delta S_{ps}^0 = \frac{(\Delta H_{ps}^0 - \Delta G_{ps}^0)}{T} \quad (3.6)$$

Mass Action Model

The equilibrium considered here is as follows:



where M^{+z} is thought to be an aggregate of j surfactant ions and $(j-z)$ firmly bound anions. The standard free energy of micellization per mole of monomeric surfactant ions is:

$$\Delta G_{ma}^0 = \frac{-RT}{j} \ln \left(\frac{f_M [M^{+z}]}{f_D^j f_A^{j-z} [D^+]^j [X^-]^{j-z}} \right) \quad (3.8)$$

When j is large, concentrations near $[CMC]$ are used and when there is no added salt, then the above equation changes to:

$$\Delta G_{ma}^0 = \left(2 - \frac{z}{j} \right) RT \ln [CMC] \quad (3.9)$$

If z is zero i.e. j counterions are firmly bound to the micelle so as to give zero charge, the above equation reduces to,

$$\Delta G_{ma}^0 = 2RT \ln [CMC] \quad (3.10)$$

If $z = j$, i.e. no counterions are bound to the micelles then equation (3.14) becomes

$$\Delta G_{ma}^0 = RT \ln [CMC] \quad (3.11)$$

Therefore, the standard heat of micellization is given by,

$$\Delta H_{ma}^0 = - \left(2 - \frac{z}{j} \right) RT^2 \frac{d \ln [CMC]}{dT} \quad (3.12)$$

3.1.4 Mechanism of Micelle Formation

The standard free energy of micellization is known to decrease with increase in chain length [32]. This indicates that with increasing chain length, there is an increase in hydrophobicity of the surfactant. Therefore, the tendency for micelle formation also increases. Further, the tendency of micelle formation is also confirmed by a high positive value of standard entropy of micellization. The explanation for positive entropy values is as follows: alkyl chains induce a structured arrangement of water molecules around themselves. When micellization starts, the alkyl chains aggregate and the structured water molecules revert to ordinary bulk conditions with a considerable increase in entropy.

3.1.5. Properties of mixed micelles

Mixtures of surfactants are often used in many industrial and technological formulations. Because the solution behaviors of these mixed surfactants can be complementary, the resulting synergism often produces properties that are better than those of their individual self-aggregates. Owing to the advantage of mixed surfactants, the structures and properties of such systems, especially those that are nonionic/ionic, have been extensively studied by various methods. But knowledge of the detailed structure and size of different kinds of mixed surfactant molecules requires further study.

CMC and Interaction Parameter of SDS/TX-100 Mixed Micelles

CMC of mixed surfactant was found by measuring surface tension of SDS/TX-100 mixed surfactant solutions at various mole fractions of SDS [8]. The ideal solution theory on mixed micelles relates the CMC of surfactant mixture (C^*) to the CMC's of pure components (C_i) and the mole fraction of the components (α_i) by

$$1/C^* = \sum_{i=1}^n \alpha_i / C_i \quad (3.13)$$

For non ideal surfactant mixtures, above equation is modified, as below, by considering the activity coefficients of components (f_i) in the mixed micelles.

$$1/C^* = \sum_{i=1}^n \alpha_i / f_i C_i \quad (3.14)$$

3.2 Ultrafiltration

Ultrafiltration refers to separation from the solvent of solute molecules which are at least 10 times bigger than solvent molecules and can be as large as 0.5μ . As the smaller solutes permeate through the membrane, the larger ones are retained. This leads to an accumulation of retained components in the boundary layer adjacent the membrane surface. This phenomenon is referred to as Concentration Polarization. Under certain conditions as the concentration of retained solute increases, large molecular weight solutes may form a 'gel', which precipitates at the membrane surface. Such a precipitate may be in the form of a cake or slimy deposit. It has the undesirable consequence of

being a secondary membrane on top of actual UF membrane. The resistance to solvent flow through this cake can be substantial so that the solvent flux is reduced.

3.2.1 Permeate Flux in UF

The permeate flux through the porous membrane can be described by *Darcy's* law for flow through porous media. It states that the volumetric flux is directly proportional to the applied pressure gradient.

$$J = \frac{1}{A} \left(\frac{dV}{dt} \right) = \frac{\Delta P}{\mu_m R_m} \quad (3.15)$$

where R_m is the intrinsic hydraulic resistance of the membrane. It is a function of pore size, tortuosity, membrane thickness, and porosity. R_m is also a function of pressure history. Therefore, membrane need compaction at a pressure higher than the highest operating pressure.

At low pressure, low feed concentrations and high feed velocity, i.e. under conditions where concentration polarization effects are minimal, the transmembrane pressure will affect flux. However, during UF of macromolecular solutes or at high pressure, the linear relationship between J and ΔP does not hold good because of concentration polarization [33], as modeled below

$$\ln \left[\frac{C_m - C_p}{C_b - C_p} \right] = \frac{J}{k} \quad (3.16)$$

From the concentration polarization model, it may be observed that the concentration of the solute at the membrane surface is considerably higher than that in the bulk. The solute concentration on the upstream side of the membrane being high and on the downstream side being very low creates an osmotic pressure difference ($\Delta\pi$). This acts in opposition to applied pressure. So in equation 3.1 (ΔP) gets replaced by ($\Delta P - \Delta\pi$).

$$J = \frac{\Delta P - \Delta\pi}{\mu_m R_m} \quad (3.17)$$

In some situations, macromolecular solutes may get adsorbed and can foul the membrane and as well can form polarized layer. These phenomenon are incorporated in the above equation by introducing the resistance due to adsorption (R_a) and resistance due to the formation of polarized layer, R_p . Therefore, the equation becomes:

$$J = \frac{\Delta P - \Delta\pi}{\mu_m (R_m + R_a + R_p)} \quad (3.18)$$

3.2.2 Real and Observed Retention

In the membrane separation, the membrane retention for a given solute is usually characterized by the intrinsic or real retention coefficient. This is defined as

$$R_r = 1 - \frac{C_p}{C_m} \quad (3.19)$$

where C_p is the solute concentration in the permeate and C_m is the solute concentration at the membrane surface (retentate side). Since it is difficult to measure C_m experimentally, it is replaced by the bulk retentate concentration C_b , which can be easily measured.

The observed retention coefficient is defined by the following equation:

$$R_o = 1 - \frac{C_p}{C_b} \quad (3.20)$$

However, the observed retention coefficient is not a property of the membrane but depends strongly on experimental conditions under which it is determined.

3.2.3. Sharp cut off UF membrane

A microporous UF membrane in which the width of pore size distribution (PSD) is small, so that the size difference between the solute which is completely retained and the solute which passed through the membrane completely unhindered is small is said to have a *Sharp Cut-off*. A microporous UF membrane, on the other hand, which has a wide size distribution is said to have *Diffuse Cut-off*. The mean pore size distribution will, however, determine the Cut-off level. Fig.3.1 depicts such types of membranes in terms of percent retention of solutes against their sizes (taken by MW).

3.3 Concentration measurement using UV- VIS spectrophotometer

According to Bouguer – Lambert – Beer (BLB) law, the absorbance at a particular wavelength for a single species is given by

$$A_\lambda = a_\lambda LC \quad (3.21)$$

where L is the cell path in cm, C is the concentration of the solute in mol l^{-1} and a_λ is the molar adsorption coefficient at wavelength λ in $\text{mol}^{-1}\text{cm}^{-1}$. The BLB law is usually valid for dilute solutions, for strongly monochromatic radiation and in optically homogeneous media. It is also valid for a mixture of absorbing species, if there are no mutual interactions, which would contravene the principle of additivity of absorbances.

Let A_1, A_2, \dots, A_n be the absorbances at wavelengths $\lambda_1, \lambda_2, \dots, \lambda_n$ for a sample containing n species. Then for $L = 1$ cm,

$$A_1 = a_{11}C_1 + a_{21}C_2 + \dots + a_{n1}C_n \text{ at } \lambda_1$$

$$A_2 = a_{12}C_1 + a_{22}C_2 + \dots + a_{n2}C_n \text{ at } \lambda_2$$

:

(3.22)

:

$$A_n = a_{1n}C_1 + a_{2n}C_2 + \dots + a_{nn}C_n \text{ at } \lambda_n$$

$a_{11}, a_{21}, \dots, a_{nn}$ may be obtained from the pure component absorbances for the n species at wavelengths $\lambda_1, \lambda_2, \dots, \lambda_n$. A_1, A_2, \dots, A_n are measured using a spectrophotometer. The equations (3.23) can be solved simultaneously to obtain the concentrations C_1, C_2, \dots, C_n of the n species.

3.4 Anionic surfactants analysis through Methylene blue method

Principle: Anionic surfactants form a complex in aqueous solution with methylene blue (cationic dye) in which then chloroform is added; thereby, transferring the complex molecule from the aqueous phase to organic phase (chloroform). The intensity of the resulting blue color in organic phase is then measured to determine the concentration of anionic surfactants [34].

Methylene blue reagent: Dissolve 100 mg of methylene blue in 100 mL of water, 30 mL of which was taken in a 1000 mL flask. Add 41 mL of 6N H_2SO_4 and 50 mg of sodium phosphate ($NaH_2PO_4 \cdot H_2O$) and dilute up to 1000 mL with water.

Wash solution: Add 41 mL of 6N H_2SO_4 into 500 mL of water in a separate 1000 mL flask. Further, add 50 g of $NaH_2PO_4 \cdot H_2O$ into the flask and shake for complete dissolution. Then dilute to 1000 mL with water.

Procedure: Take 100 mL sample solution in a separating funnel. Make alkaline by dropwise addition of 1N NaOH, using phenolphthalein as indicator. Then add 1N H_2SO_4 , dropwise, until pink color disappears. Add 10 mL of $CHCl_3$ and 25 mL of methylene blue reagent. Shake funnel vigorously for 30 seconds and let the phase separation to carry out. Excessive agitation may cause formation of emulsion. In order to avoid persistent formations of emulsions, add a small volume of isopropyl alcohol (<10 mL); any chosen volume, however, should be similar in any other sample analysis. Draw off $CHCl_3$ layer and repeat extraction couple of times, using 10 mL of $CHCl_3$ each time. Rinse the

delivery tube of separating funnel with small amount of chloroform. Transfer all the CHCl_3 extracts in another separating funnel. Add 50 mL of wash solution (earlier prepared) and shake vigorously for 30 seconds. Allow it to settle and draw off CHCl_3 layer filtering through a funnel (using glass wool) into a 100 mL volumetric flask; extract must be clear. Extraction of wash solution is repeated twice; adding 10 mL CHCl_3 each time and add then filtering through glass wool. Rinse glass wool and funnel with CHCl_3 . Dilute the filtrate up to 100 mL with CHCl_3 and mix well. Determine the absorbance of this filtrate at 652 nm (wavelength) against blank reading of CHCl_3 . Unknown sample concentration can be then be calculated using calibration curve. The maximum concentration that can be measured using this method is 2 ppm.

In this method consumption of chloroform (toxic and having suspected carcinogen affect) is high. Further, time required for analysis of one sample is also large.

Rapid determination by modified method:

Acidic Methylene blue standard solution: Methylene blue of 0.35 g was dissolved in pure water and 6.5 mL of concentrated sulfuric acid was added. This solution was diluted to one liter to make 1 mM methylene blue solution.

Procedure: A water sample of 50 mL is placed in a separating funnel; then 5 mL of a 1 mM methylene blue solution and 10 mL of chloroform are added. The mixture is then shaken vigorously for 1 min. The separating funnel is allowed to stand for 1 min, and then chloroform phase is drawn off simply from funnel. Absorbance of chloroform phase is measured at 652 nm wavelength [35].

The maximum concentration that can be measured through this method is also 2 ppm. In this method, only 10 mL of chloroform is required and time for analysis is also low.

Since, the present work deals with a mixture of surfactants (SDS & Triton-X100), it was, therefore, thought appropriate to observe influence of one surfactant over other while determining their respective concentrations through two separate procedures (methylene blue for SDS & UV at 278 nm for Triton). Fig.3.2 and Fig.3.3 depict such calibration curves. There is very marginal difference observed in SDS analysis through methylene blue method, in presence of Triton; whereas, there is no effect of presence of SDS during measuring concentration of Triton by UV analysis.

3.5 Multi objective optimization:

As name suggests, a multi-objective optimization problem (MOOP) deals with more than one objective functions. Because of a lack of suitable solution methodologies, an MOOP has been mostly cast and solved as a single-objective optimization problem in the past.

Many real-world engineering design or decision-making problems involve simultaneous optimization of multi objectives. The principle of multi-criterion optimization is different from that in a single-objective optimization. In single-objective optimization, the goal is to find the best design solution, which corresponds to the minimum or maximum value of the objective function. On the contrary, in multi-criterion optimization with conflicting objectives, there is no single optimal solution. The interaction among the different objectives gives rise to a set of compromised solutions, largely known as the Pareto-optimal solutions. Since none of these Pareto-optimal solutions can be identified as better than others without any further consideration, the goal in a multi-criterion optimization is to find as many Pareto-optimal solutions as possible. Once such are found, it usually requires a higher-level decision-making with other considerations to choose one of them for implementation [36]. In dealing with multi-criterion optimization problems, classical search and optimization methods are not efficient, simply because

- Most of them cannot find multiple solutions in a single run, thereby requiring them to be applied as many times the number of desired Pareto-optimal solutions.
- Multiple applications of these methods do not guarantee finding widely different Pareto-optimal solutions.
- Most of them cannot efficiently handle problems with discrete variables and problems having multiple optimal solutions. On the contrary, the studies on evolutionary search algorithms, over the past few years, have shown that these methods can be efficiently used to eliminate most of the above difficulties of classical methods. Since they use a population of solutions in their search, multiple Pareto-optimal solutions can be found in one single run.

The Non-dominating Sorting Genetic Algorithm (NSGA) proposed by Srinivas and Deb [37] was one of the first such evolutionary algorithms. Over the years, the NSGA have been criticized for its high computational complexity, non-elitism approach and the need of specifying a sharing parameter. An improved version of NSGA is NSGA-II [38] in which the above difficulties can be eliminated.

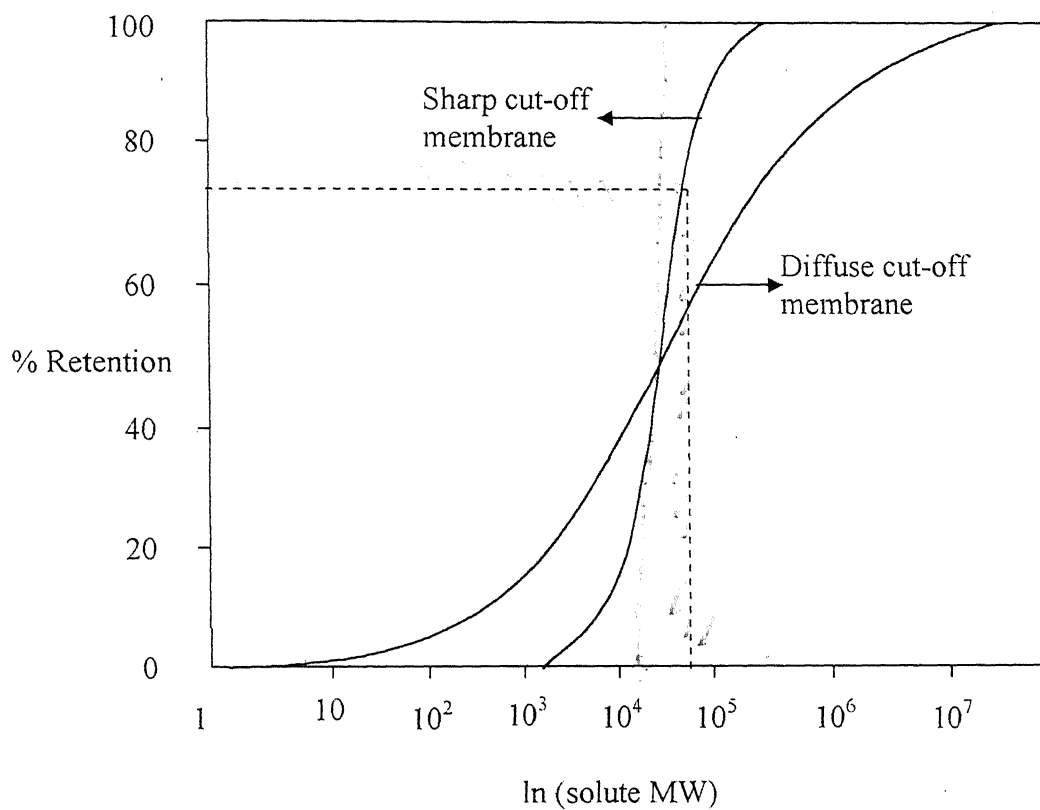


Fig.3.1 Percent retention vs. $\ln(\text{solute MW})$

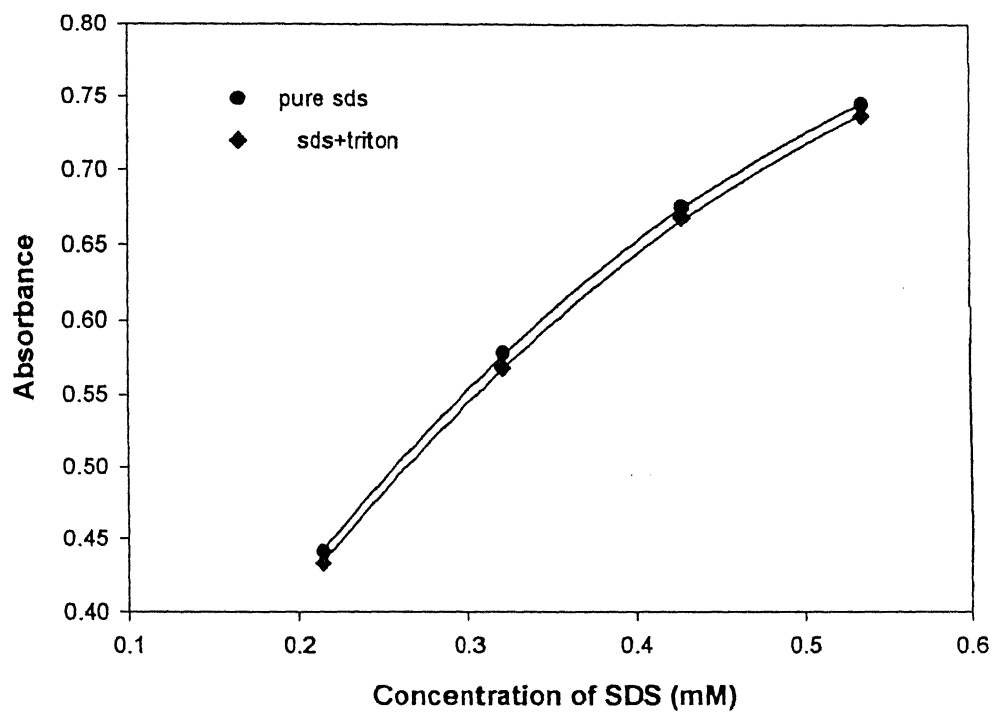


Fig.3.2 Effect of Triton X-100 on SDS analysis

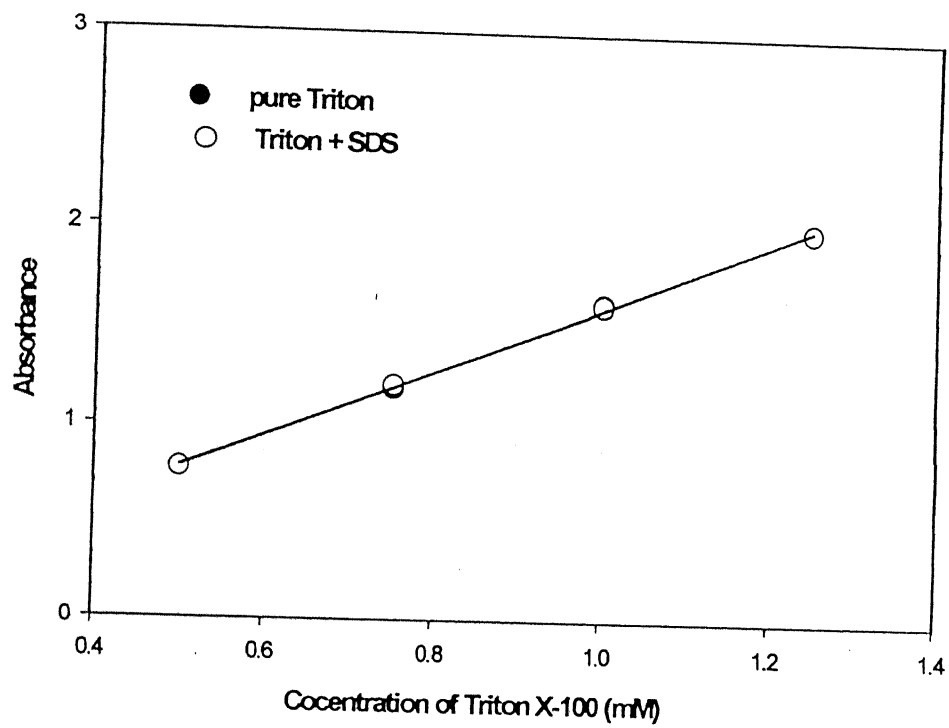


Fig.3.3 Effect of SDS on Triton analysis

4.1 Membrane and Chemicals

Membrane

Type : GR90PP; Danish Separation Systems, Denmark
Diameter : 76 mm
MWCO : 5,000
pH, Temperature, Pressure Range: 1 – 13, 0 -75°C, 0 – 145 psi

Chemicals

- a) Sodium dodecyl sulphate (SDS) was obtained from BDH, Mumbai.
- b) Triton X-100 of purity 98.1% was obtained from FINE-CHEM LTD, Mumbai
- c) Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ of 98.5% was obtained from Qualigens Fine Chemicals, Mumbai.
- d) Methylene blue was obtained from Qualigens Fine Chemicals, Mumbai.
- e) Chloroform, CHCl_3 , of purity 99.7% was obtained from Qualigens Fine Chemicals, Mumbai.
- f) NaOH of purity 97% was obtained from Qualigens Fine Chemicals, Mumbai.
- g) Sulphuric Acid, H_2SO_4 , of purity 98 % was obtained from Qualigens Fine Chemicals, Mumbai.
- h) Sodium phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) of purity 98% was obtained from Qualigens Fine Chemicals, Mumbai.
- i) Isopropyl alcohol of purity 98% was obtained from Qualigens Fine Chemicals, Mumbai.
- j) Phenolphthalein indicator was obtained from FINE-CHEM LTD, Mumbai
- k) Glass wool was obtained from LOBA CHEMIE , Mumbai

4.2 Instruments and other auxiliaries

UF CSTR Cell Specification

UF CSTR cell was designed and manufactured at the workshop in IIT, Kanpur.

Material of Construction	: SS – 316
Total useful volume	: 400 ml
Residual Volume	: 100 ml
Maximum Operating Pressure	: 250 psi

Stirrer Characteristics

Diameter of the stirrer	: 0.045 m
Height of the stirrer above the membrane	: 0.03 m

Reservoir Specifications

Diameter	: 100 mm
Length	: 200 mm
Capacity	: 1 L

Stirrer Motor (geared motor ac/dc motor) with range (Supply: 24V; Amperage: 12A; & 6V and 12A Horse Power: 0. 025 Hp: RPM: 26, 35, 45, 60)

Compressor (Type: VDE 0530) with range (Supply: 220V, 1 Phase, 50 Hz; Amperage: 2.6 A; Wattage: 180 W)

Weighing Balance

Model	: Afcoset Electronic Balance
Accuracy	: 0.0001 g
Maximum Weight	: 180 g

VIS – UV Spectrophotometer

Model	: UV – 1601, Shimadzu Corporation, Japan
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Atomic Absorption Spectroscopy

Model	: 220FS VARIAN
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4.3 Description of CSTR experimental setup

To carry out the ultrafiltration operation with surfactants in continuous stirred tank reactor mode, setup was fabricated. Schematic diagram of setup is shown in Fig.4.2. It is atomized using sensors. There is a reservoir (2) of one liter capacity in which feed solution will be filled. This reservoir is connected to UF cell (1) of 400 mL capacity (with stirrer) as shown in figure. There are 2 solenoid valves (for liquid flow) and four pneumatic valves (for air flow, which are backside, not shown in figure). One solenoid valve (3 in figure) is to flow feed solution into UF cell from reservoir and another (4 in figure) is for recycling the retentate from UF cell to reservoir. Valve (5), as shown in figure, in recycling line controls the recycling flow rate of retentate solution. There are two air regulator valves (6 and 7 in figure) to regulate the applied pressure for UF cell and reservoir respectively. As shown in figure, 10, 11 and 12 are sensors which controls pneumatic valves. There are two pressure releasing pneumatic valves, one for UF cell and one for reservoir. Similarly there are two pressurizing pneumatic valves (back side). As soon as experiment is started with feed solution in reservoir, feed flow into the UF cell. Whenever solution reaches level-1 (shown in figure), UF cell will be pressurized and pressure is released from reservoir (flow will be stopped from reservoir to UF cell). At the same time flow of retentate will start from UF cell to reservoir at adjusted flow rate. This retentate flow rate is adjusted to 15-20 mL/min so that feed solution in the UF cell is recycled frequently in regular intervals to maintain the feed concentration constant through out the experiment. Whenever level in UF cell reaches level-2 (shown in figure), pressure will be released from UF cell (recycling will be stopped) and reservoir is pressurized automatically to flow feed solution from reservoir to UF cell. These operations will continue until experiment is in automatic mode. If solution level in reservoir reach level-3 (reservoir is completely empty), then automatically experiment will be stopped. Permeate is collected until process reaches steady state.

4.4 Design of Experiments

Experiments were designed to observe SDS and Triton X-100 surfactant mixture retention characteristics by varying applied pressure and total feed surfactant concentration in batch mode and continuous mode. The ratio of SDS and Triton X-100 was fixed at 7:3 through out the entire work. The permeate flux and concentration were measured as function of time at various total feed surfactant concentrations and pressures. Retention characteristics of mixed surfactants were studied by taking 3 different total feed concentration (10mM, 25mM and 50mM) at 4 different pressures (480 kPa, 551 kPa, 629 kPa and 758 Kpa). For optimization of operating conditions of CSTR mode UF cell (total feed concentration and pressure), best-fit equations were developed for permeate flux and retention of surfactant as function of pressure and total feed concentration. NSGA-II was used for optimization. Then total feed surfactant concentration and pressure were held constant (optimized conditions) for removal copper. Retention of copper was observed at different feed concentrations of copper (2 mM, 3 mM and 4 mM)

4.5 Experimental Procedure

A fresh membrane was placed on the porous support of the UF cell shown in the Fig.4.1. The cell was then assembled and filled with distilled water. Initial compaction of the membrane was carried out. For this purpose, the cell was pressurized using an air compressor and the flux was measured as a function of time. The operation was carried out at a pressure of 952 kPa for six hours. Constancy of water flux during this period suggested that no further compaction was necessary. The selected compaction pressure was higher than the highest operating pressure to ensure no compaction during the actual experimental work. For estimation of R_m , the pressure was then varied and the flux was recorded as a function of applied pressure. The hydraulic membrane resistance was obtained from the linear relationship of pressure vs. flux data.

4.5.1 Batch Mode

For experimental runs in batch mode UF cell, as shown in Fig.4.1, the cell was dismantled and the membrane was rinsed with distilled water and placed on porous

support. The test solution was poured in the cell. It was pressurized and the permeate flux was measured at regular intervals until steady state obtained. Permeate concentration of the SDS and Triton X-100 surfactants were measured using methylene blue method and VIS – UV spectrophotometer respectively.

4.5.2 CSTR Mode

For experimental runs in continuous mode UF cell, as shown in Fig.4.2, feed solution has been taken in the reservoir and membrane was placed on porous support in the UF cell. Air regulator was adjusted to required pressure value. As explained earlier in section 4.3, every valve is automatically controlled except recycling flow rate of retentate solution (manually controlled). Permeate was collected in regular intervals until process obtains steady state and concentrations of SDS and Triton X-100 in permeate were measured through methylene blue method and VIS – UV spectrophotometer respectively.

Under optimized conditions of mixed surfactants, MEUF experiments were carried out with copper solution and permeate flux was measured at regular intervals. Permeate concentration of copper was measured using Atomic absorption spectroscopy (AAS) at 324 nm of wavelength.

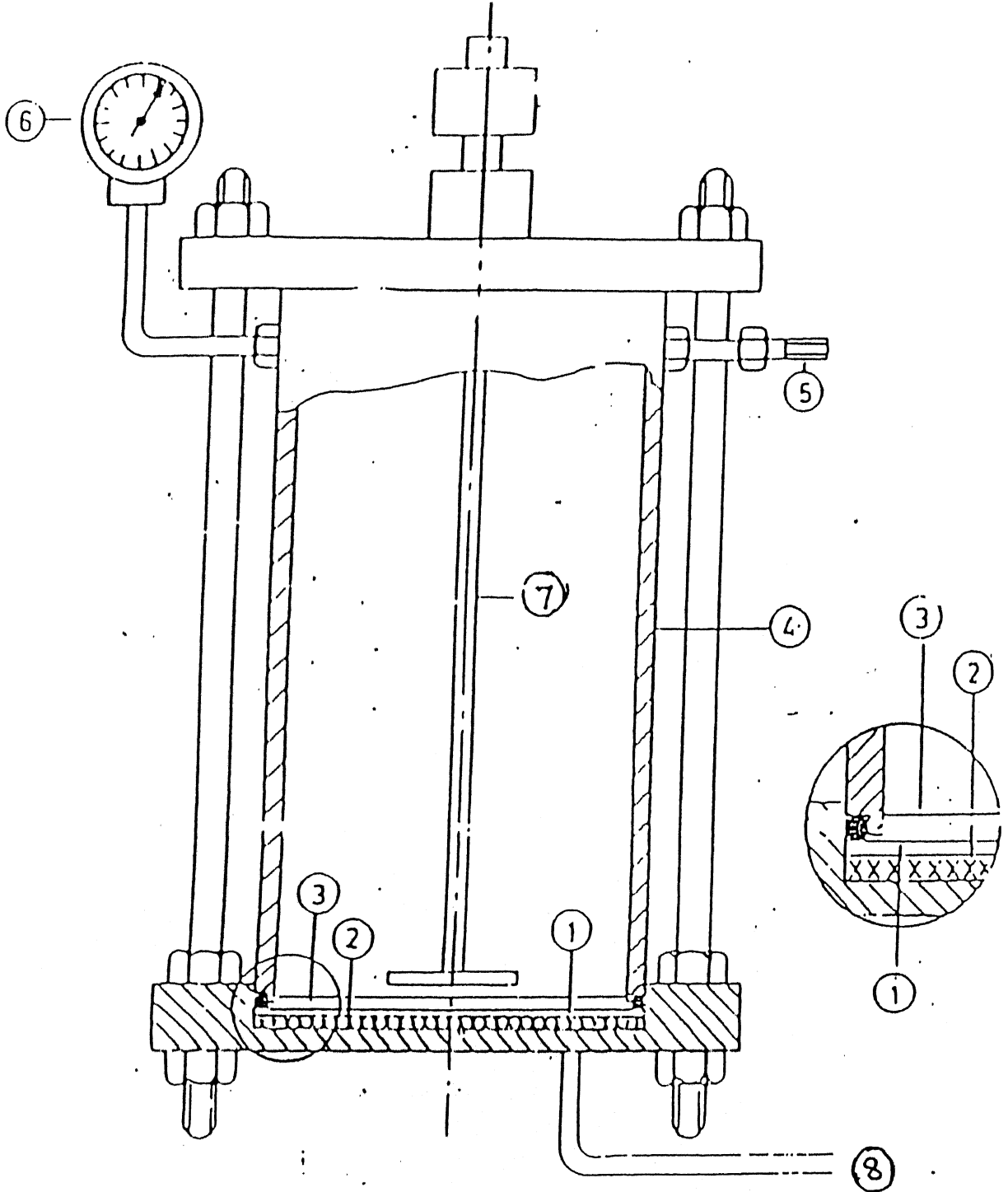


Fig. 4.1 Ultrafiltration Cell

1. Membrane 2. Porous Support 3. 'O' Ring 4. Cell Body 5. Pressure line Connector 6. Pressure Gauge 7. Stirrer 8. Sample Outlet

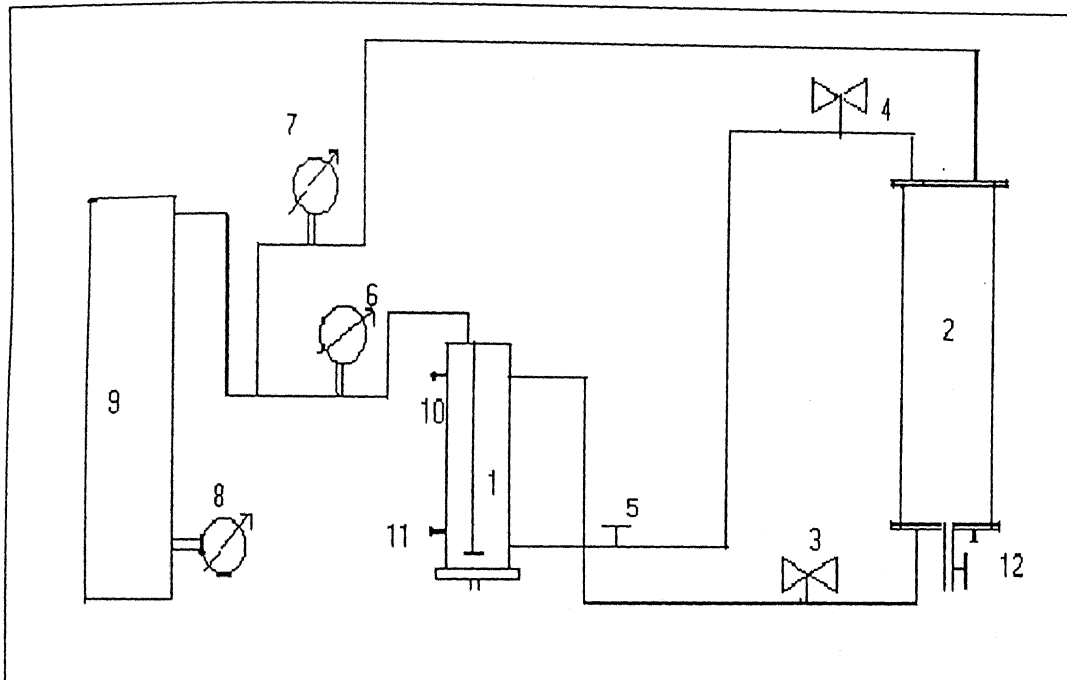


Fig.4.2 CSTR mode ultrafiltration cell

- 1. Ultrafiltration cell
- 2. Reservoir
- 3&4. Solenoid valves
- 5. Recycling line valve
- 6, 7, &8. Pressure gauge
- 9. Air compressor
- 10. Level-1 sensor
- 11. Level-2 sensor
- 12. Level-3 sensor

Fig.4.3 Photographs of CSTR mode Ultrafiltration experimental setup

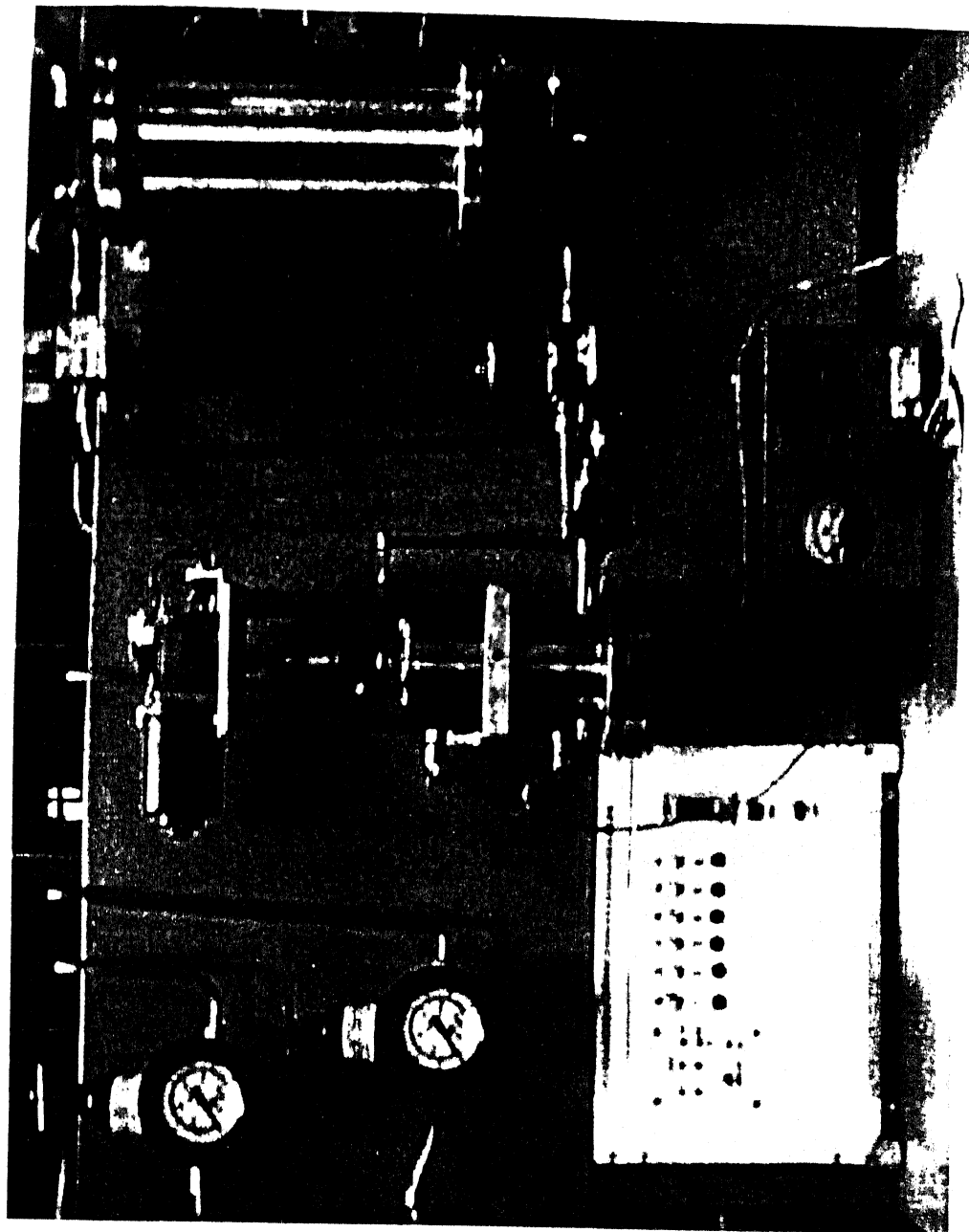


Fig.4.3a Complete setup

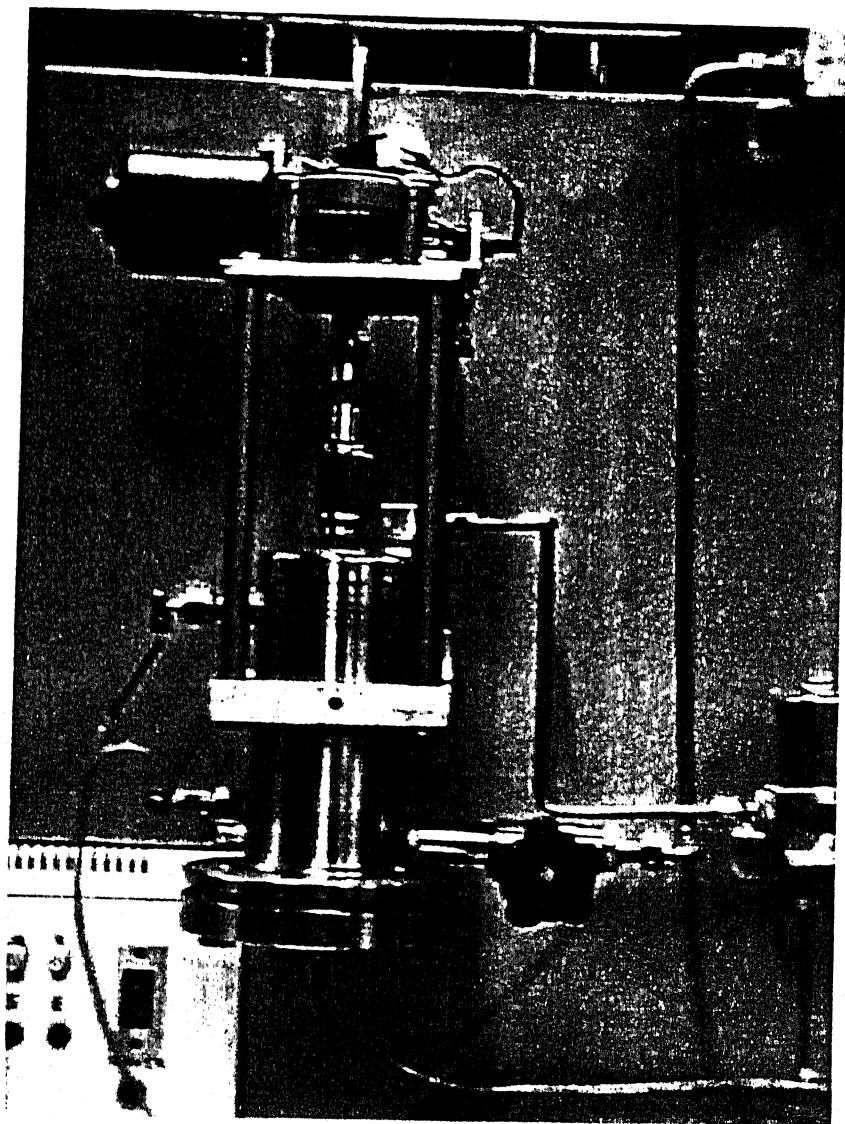


Fig.4.3b UF cell in CSTR Mode

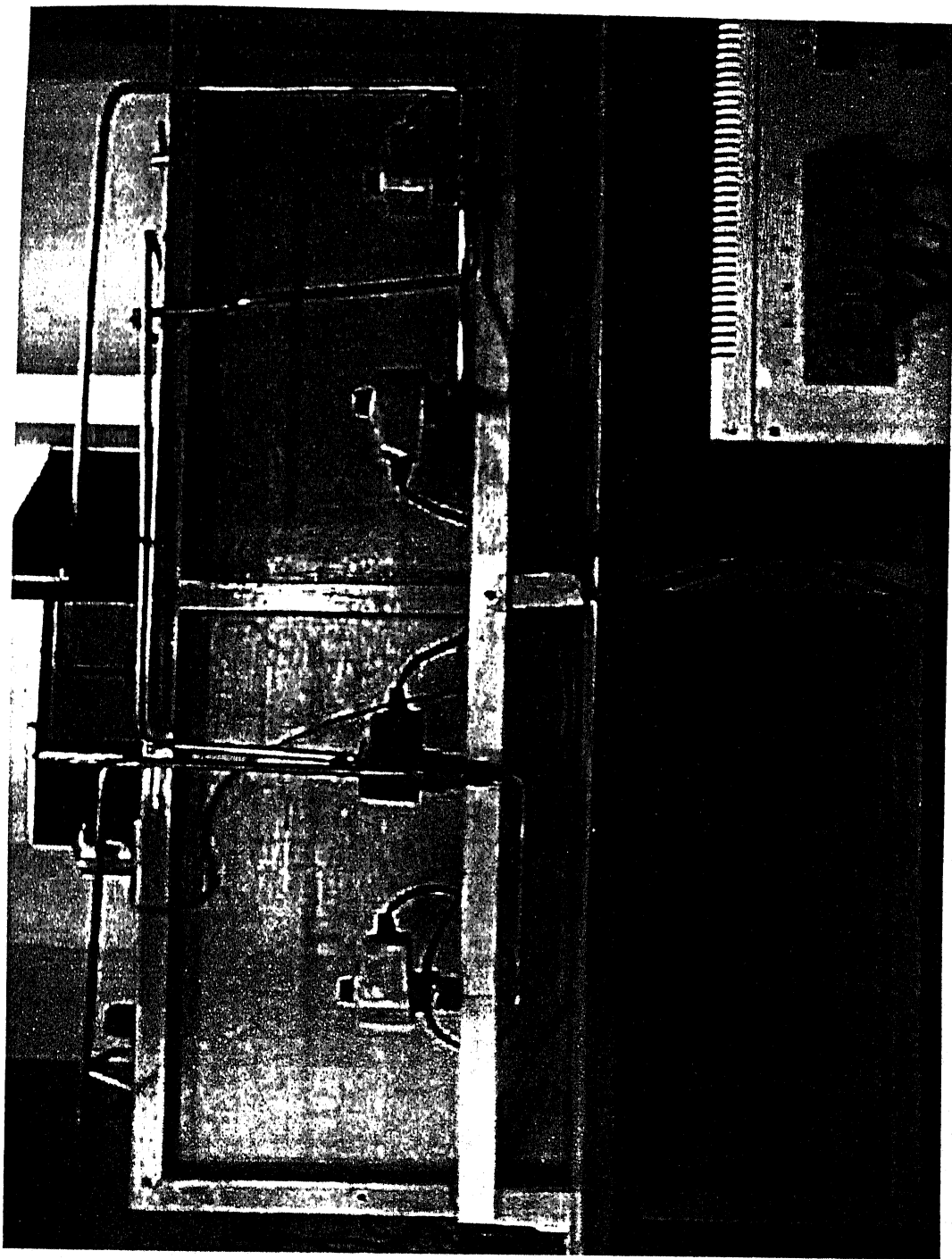


Fig.4.3c Pneumatic valves

RESULTS AND DISCUSSIONS

Micellar enhanced ultrafiltration experiments were conducted to study the characteristics of the operation in a continuous stirred tank reactor mode UF cell using SDS (anionic) and Triton X-100 (nonionic) surfactants mixture in 7:3 ratios, respectively. The objective is to specifically study the effects of operating conditions, such as pressure and total surfactant concentration, on permeate flux and surfactant retention. These operating conditions were optimized using a powerful tool (non-dominated sorting genetic algorithm, NSGA-II). The arrived optimized conditions may be used for removal of a metal ion existing, in cationic form, from an aqueous solution. In this work, copper ion has been selected for such a case study of metal ion removal under optimized operating conditions of MEUF studies, using exclusively pure surfactants mixture.

5.1 Selection of membrane and MEUF Operating Conditions

A 5000 MWCO (sharp cut-off, refer to section 3.2.3) UF membrane was selected for MEUF experimental study. Since, the membrane, obtained for experimental purpose of sharp cut-off by nature; therefore, by definition, if the solute (lowest micelle which may be approximately 15000 MW for the present work) that has to be removed more or less completely, by the membrane, then the peak pore size of the membrane should be slightly smaller than the minimum size of micelle. A membrane of 5000 MWCO may generally have a peak point of 12000 MW opening; therefore, this supports the selection of the MWCO membrane, in terms of retention of minimum size micelle. In general, MWCO of the membrane should be much lower than the average size of micelles formed (SDS and Triton X-100 in 7:3 ratio) during the entire range of surfactants concentrations. Further, the membrane was selected on the basis of compatibility (as per the specifications provided by the manufacturer).

Operating pressure range was selected as 482 kPa to 758 kPa, so as to obtain a sufficient rate. Further, the minimum pressure value was selected to overcome osmotic

pressure of CMC of surfactant mixture; the value of which was approximately estimated and was found to be much smaller than 482 kPa. In batch mode UF cell (without stirring) experiments were conducted with pure SDS surfactant and with mixture of SDS and Triton X-100 surfactants in the ratio of 7:3, respectively, at constant pressure of 620 kPa. These experiments were carried out with the aim to study the characteristics of MEUF with starting feed surfactant concentration below and above CMC; obviously, therefore, it was carried out to study the influence of change in feed concentration as a function of time on retention characteristics.

Yu-Min Yang worked [7] upto 10 mM of total surfactant concentration and achieved 85% removal of copper. In order to observe the influence of further values of surfactant concentrations on percent removal of copper, the total feed surfactant concentration was varied from 10 mM to 50 mM.

A low stirring (constant) speed was maintained though out the experimental work. This was done to avoid the breakage of micelles into dimmers and trimmers. All the experiments were carried out at room temperature. However, values of fluxes were corrected with respect to change in room temperature by measuring hydraulic resistance of membrane (R_m) of membrane through incorporating and including the viscosity of water for R_m estimation at different temperature.

5.2 Micellisation and ultrafiltration of surfactant solution:

Permeate flux and its concentration were measured and analyzed as a function of time, so as to observe the influence of change in feed concentration as a function of time.

5.2.1 Batch mode UF cell study

Pure SDS surfactant retention characteristics

Experiments were conducted with pure SDS surfactant in batch mode UF cell without stirring at constant pressure of 620 kPa and starting feed concentration was varied below and above CMC level. SDS forms micelles at its CMC value of 8.0 mM, which is relatively a higher value compared to other types of surfactants. Starting feed concentration was varied from 6 mM to 200 mM. Fig.5.1 shows all the values of flux variation with time for different feed concentration. The figure depicts mild exponential

decline of permeate flux with time. Further, it is observed that as the starting feed concentration increases, the exponential decline rate decreases. This is because with low values starting feed concentration, there is a build up process and formation of micelles as a function of time. This build up of micelles, therefore, during MEUF leads to formation of micellar aggregation layer (MAL) which acts as additional resistance against to the flow through the membrane. Thus, flux declines as a function of time and the rate of exponential decline become higher with low starting feed concentration. Further, obviously the values of flux were more with low feed concentration compared to values with high feed concentration. Fig. 5.2 depicts the retention behaviour for above mentioned experiments. Percent retention values were found to be higher with increase in feed concentration. There were little decline of percent retention as a function of time, particularly under higher feed concentration. It is clearly evident that retention values are very low with starting feed concentration lower than CMC value. It is understandable as below CMC, there is no formation of micelles and hence monomers of surfactants only exist in the bulk solution. Since, monomers passage rate through the membrane may not be equal to water, there is a build up of concentration polarized layer which not only retards flux rate, also retards free passage to all monomers. This gives rise to some values of percent retention; however, should be lower than other cases with feed concentration higher than CMC. The size of monomer is much smaller than the membrane pore size.

SDS and Triton X-100 surfactants mixture retention characteristics

As stated earlier, surfactants are the key components in MEUF process; the process is economical if the surfactant consumption is minimized. One of the ways to minimize the consumption is to decrease the value of CMC by using mixture of surfactants. SDS surfactant molecules are charged molecules and are small in length which create high electrostatic repulsive forces and sets its CMC to a high value (8 mM). Therefore, the addition of small amount of nonionic surfactant, like Triton X-100, reduces these repulsive forces causing shielding effect which significantly reduces the mixture CMC value ($\sim 0.63\text{mM}$) [8].

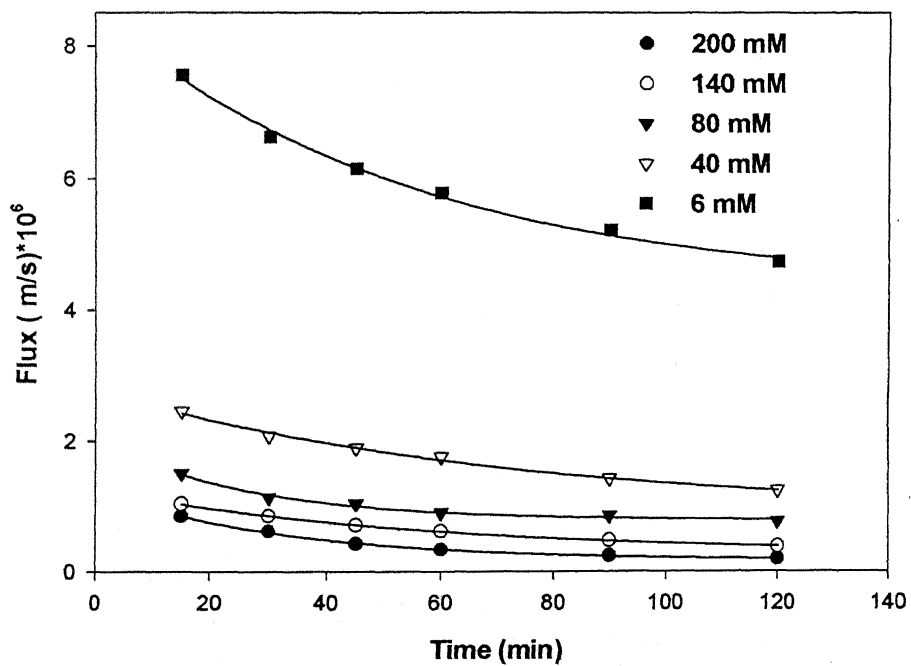


Fig.5.1 Variation of flux with time in batch mode at various SDS concentration at 620 kPa

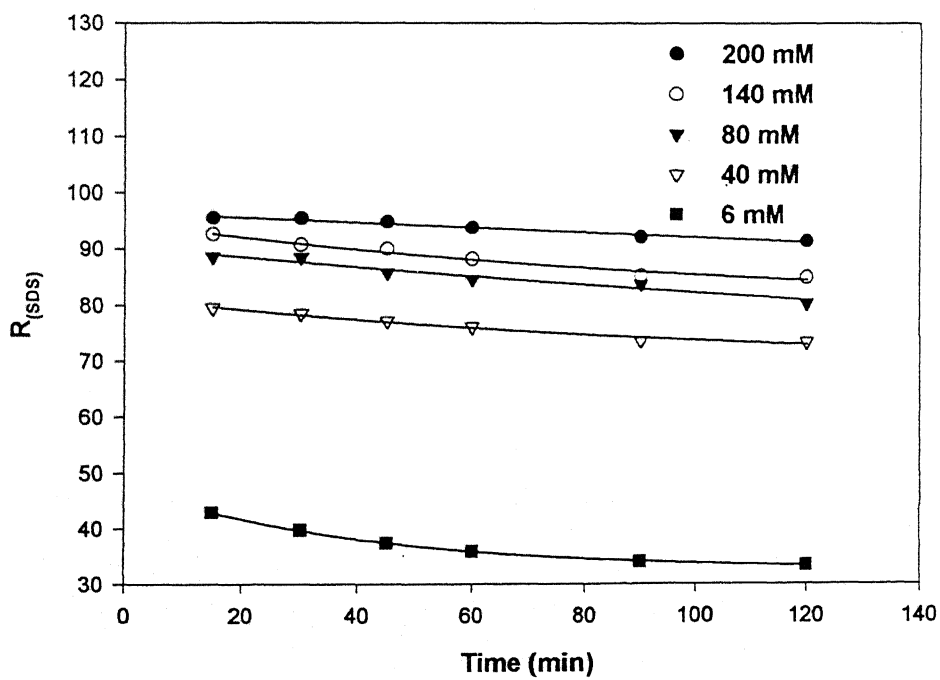


Fig 5.2 Variation of $R_{(sds)}$ with time in batch mode at 620 kPa

Further, it was found that the mixture of SDS and Triton in 7:3 ratios, respectively, was the most suitable ratio to form mixed micelles [7]. Therefore, in this work, all experiments with mixed surfactant were carried out with this ratio of 7:3.

Fig.5.3 shows the decline of permeate flux with time due to formation of MAL. Figures 5.4, 5.5 and 5.6 have been drawn to depict percent retention of SDS, Triton and the total mixture against time from a single experimental run. It is clear that Triton percent retention is higher than SDS percent retention. Comparing Fig.5.2 and Fig.5.4, one may observe that there is more or less no difference in percent retention values of SDS which itself is an advantage (as CMC of pure SDS is much higher and hence could have given much higher retention; as increase of concentration increases percent retention), apart from reduction in CMC value.

5.2.2 Continuous stirred tank reactor (CSTR) mode UF cell study

Experiments were carried out in CSTR UF cell with mixed surfactants and MEUF characteristics were studied by varying applied pressure and total feed surfactant concentration at constant stirring speed.

Effect of pressure on permeate flux and surfactant retention

Fig.5.7 to Fig.5.9 show the variation of permeate flux with time at various pressures and using varying total feed concentrations. It was observed that the permeate flux remains constant with time, suggesting negligible effect of concentration polarization. Fig.5.10 depicts the variation of such constant permeate fluxes against pressure at different total feed concentrations. Linear variations of fluxes with pressure confirmed the absence of MAL and concentration polarization effects.

Fig.5.11 to Fig.5.19 shows the variation of SDS, Triton X-100 and total surfactants mixture retentions with time. Retention is exponentially decreasing with time and after around two hours steady state retention values were observed. This is because of breakage of micelles during early stages of MEUF operation while the feed is continuously flown and exited through the UF cell. Further, retention values were found to be higher than the values obtained under batch mode (refer Fig.5.6).

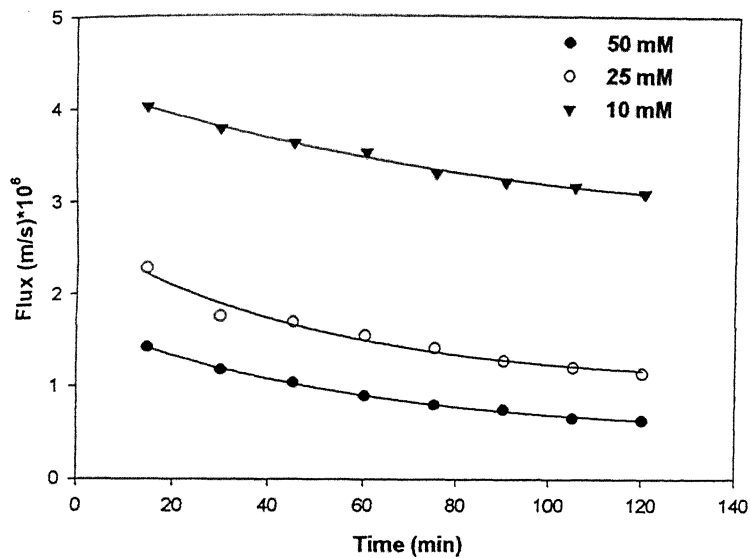


Fig.5.3 Variation of flux with time in batch mode at 620 kPa with SDS and TX-100 in 7:3 ratio

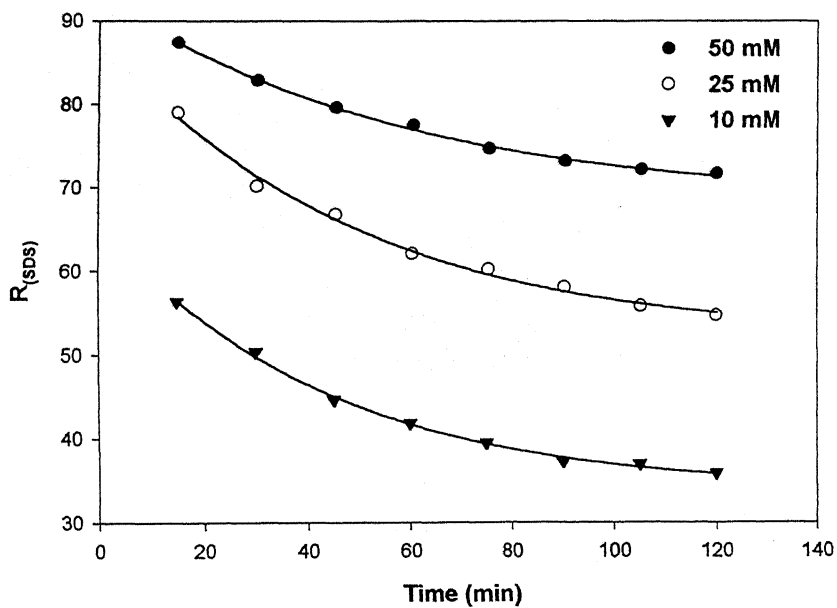


Fig.5.4 Variation of $R_{(sds)}$ with time in batch mode with SDS and TX-100 in 7:3 ratio

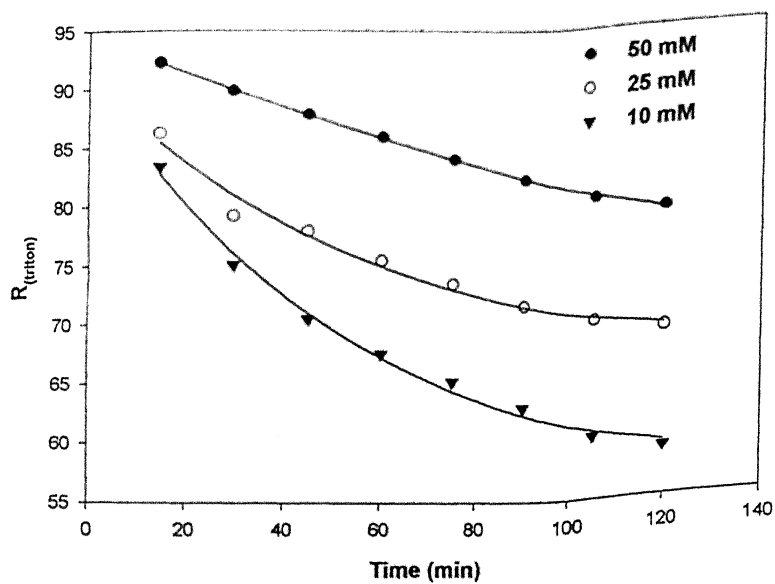


Fig.5.5 Variation of $R_{(triton)}$ with time in batch mode with SDS and TX-100 in 7:3 ratio

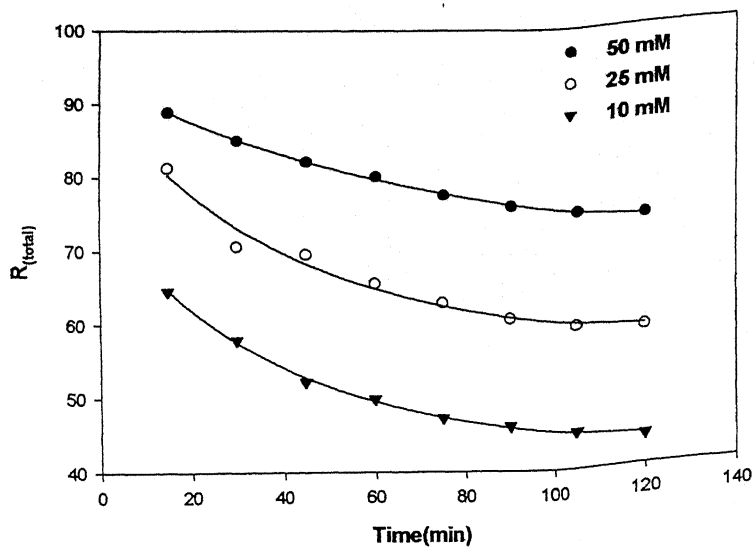


Fig.5.6 Variation of $R_{(total)}$ with time in batch mode with SDS and TX-100 in 7:3 ratio

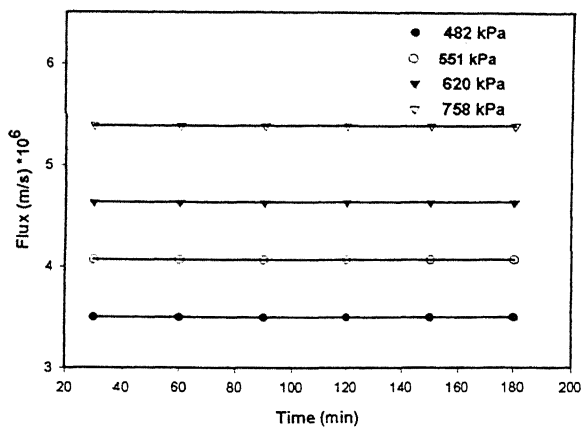


Fig.5.7 Variation of permeate flux with time at total feed conc. of 10 mM in CSTR

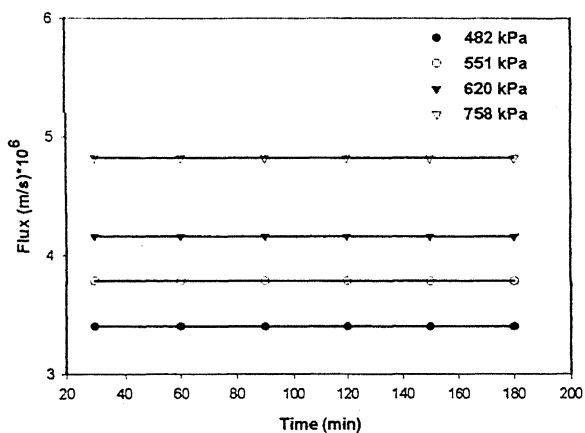


Fig. 5.8 Variation of permeate flux with time at total feed conc. of 25 mM in CSTR

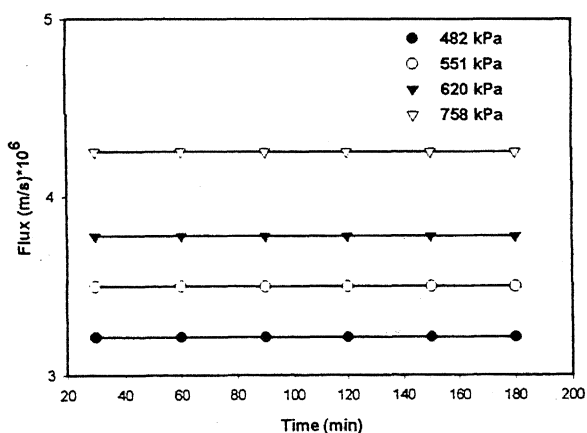


Fig. 5.9 Variation of permeate flux with time at total feed conc. of 50 mM in CSTR

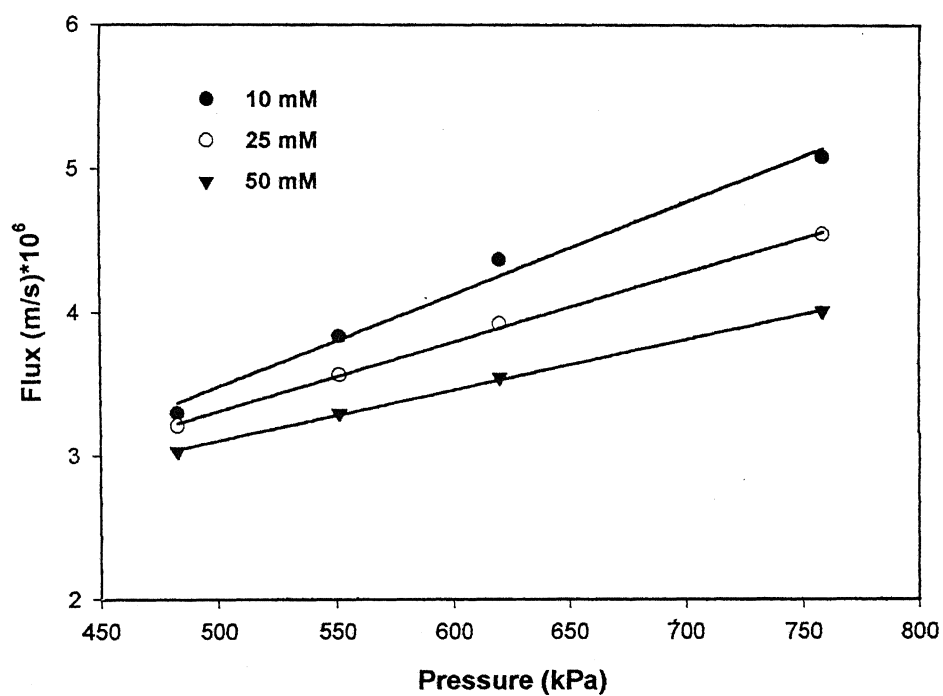


Fig.5.10 Variation of permeate flux with pressure

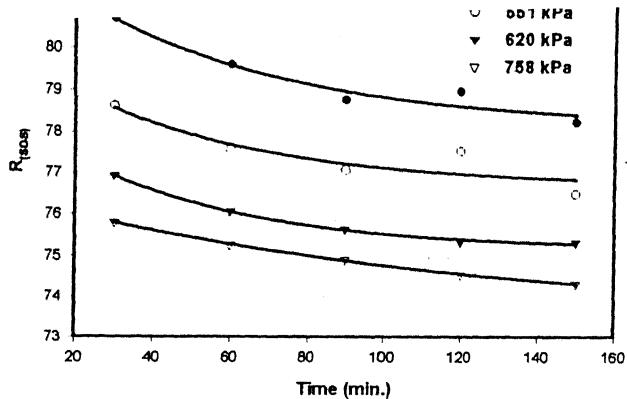


Fig. 5.11 Variation of $R_{(sos)}$ with time at 10mM total surfactant conc.

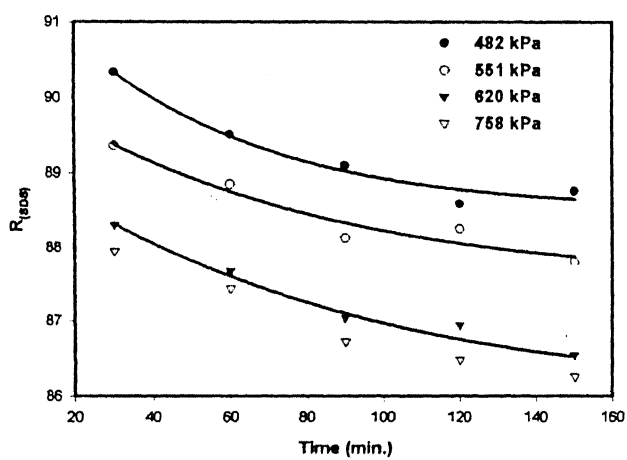


Fig. 5.12 Variation of $R_{(sos)}$ with time at 25 mM total surfactant conc.

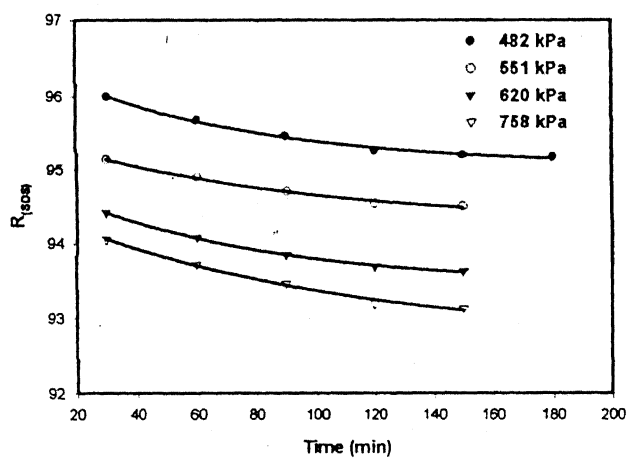


Fig. 5.13 Variation of $R_{(sos)}$ with time at 50 mM total surfactant conc.

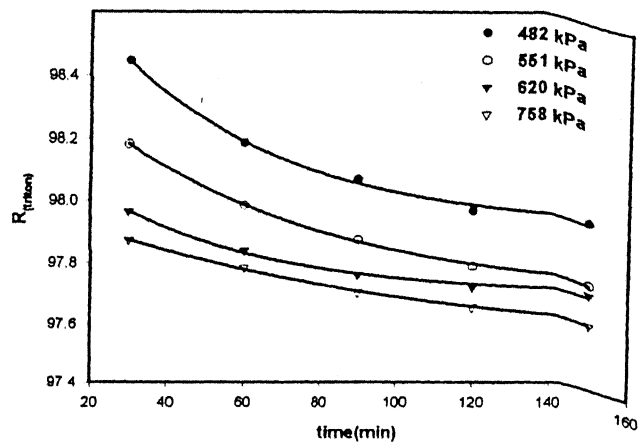


Fig.5.14 Variation of $R_{t(tion)}$ with time at 10 mM total surfactant conc.

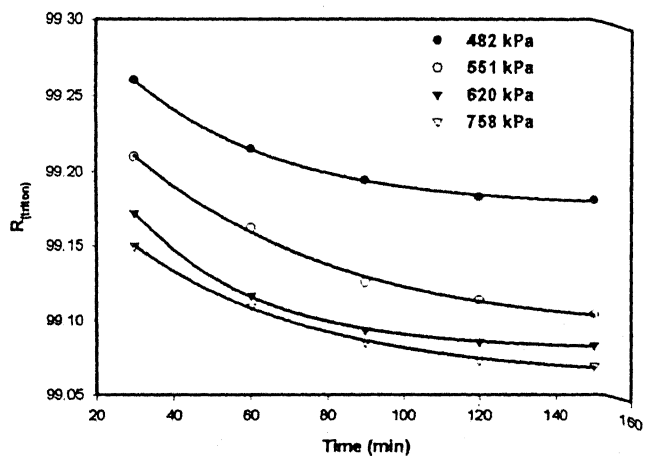


Fig.5.15 Variation of $R_{t(tion)}$ with time at 25mM total surfactant conc.

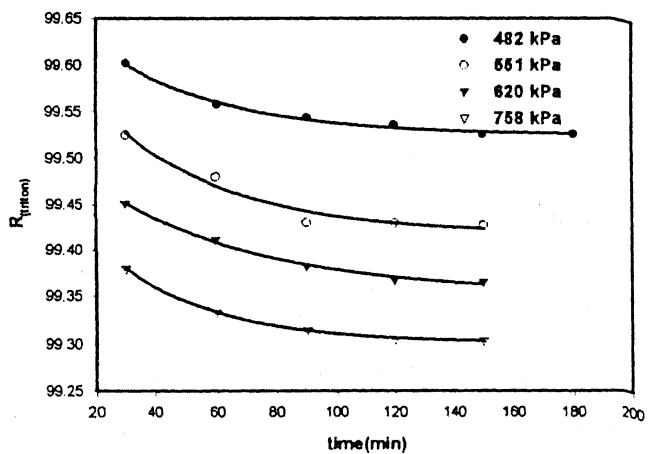


Fig.5.16 Variation of $R_{t(tion)}$ with time at 50mM total surfactant conc.

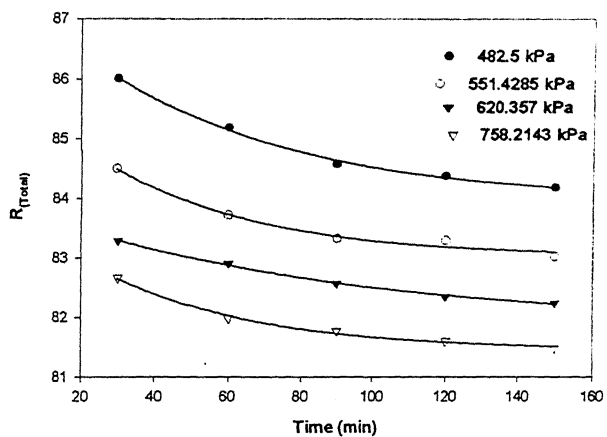


Fig.5.17 Variation of $R_{T(\text{Total})}$ with time at 10 mM of total feed conc.

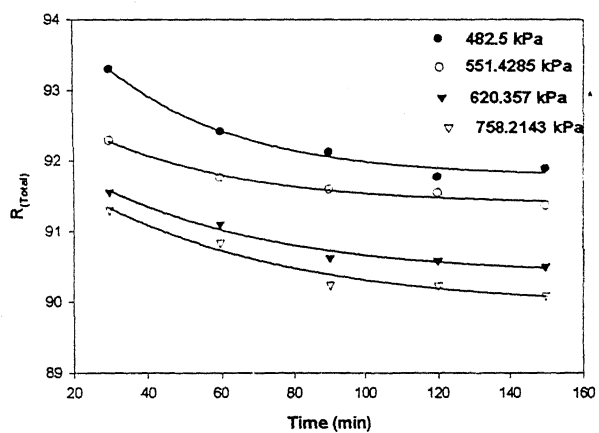


Fig.5.18 Variation of $R_{T(\text{Total})}$ with time at 25 mM of feed total conc.

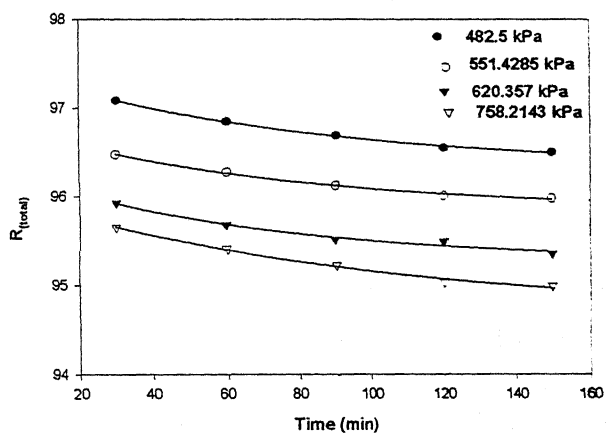


Fig.5.19 Variation of $R_{T(\text{Total})}$ with time at 50 mM total feed conc.

This is because of the formation of dimmers and trimmers of surfactant molecules during MEUF operation and their gradient across the membrane being larger in batch process. Fig. 5.20 to Fig.5.22 were drawn between steady state retentions of SDS, Triton and total surfactants and pressure gradient respectively. Although, there is a decreasing trend of retention with increasing pressure, the same may be also considered to be of not much of variation, especially with higher feed concentration. Slight amount of variation may be attributed to breakage of micelles with increasing pressure.

Effect of total feed concentration on permeate flux and surfactant retention

Variation of steady state flux with total feed surfactant concentration has been shown on Fig.5.23, at different pressure. There is little decline in flux with increase in concentration. As stated earlier that during MEUF operation no effect of concentration polarization was observed and therefore this slight decline of flux may be simply attributed to increase of solution viscosity. With increasing feed concentration, number and size of micelles also increases. Further, it was discussed earlier that the formation of MAL in CSTR mode is almost negligible; therefore, the flux variation with feed concentration is much lower compared to batch operation which is now plotted for comparison purpose and shown in Fig.5.24 & Fig.5.25.

CSTR mode results for variations of SDS, Triton and total retentions on total feed concentration are as shown in Fig.5.26 to Fig.5.28. These values of retentions exponentially increase with increase in total feed concentration. Since, permeate concentration does not depend significantly on total feed concentration, as any extra mass addition of surfactants will only increase the number of micelles, keeping the bulk concentration in the feed side always at CMC level. Therefore, if percent retentions are based on feed side bulk concentration (excluding micelles) then there should not be variation of retention with increase in feed concentration. However, in the present work, feed concentration was consistently taken on the basis of total mass of surfactants addition, disregarding the formation of micelles with any extra mass beyond CMC level. Therefore, there is exponential rise of retentions with increase in feed concentration.

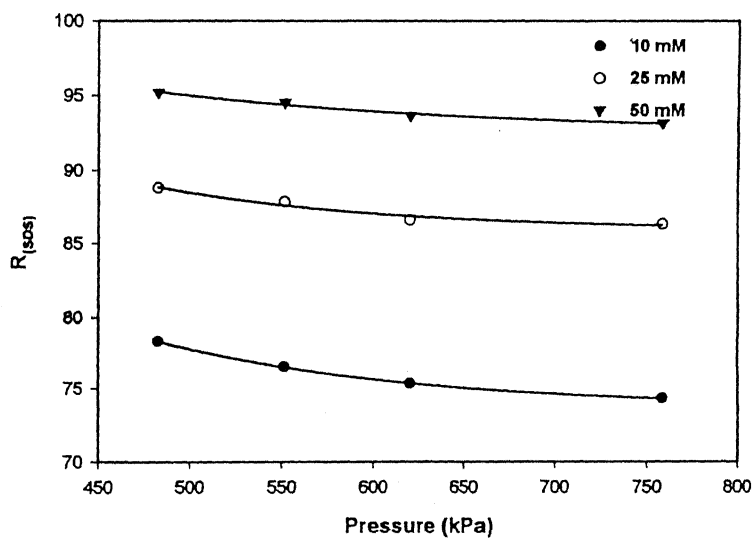


Fig.5.20 Variation of $R_{(sds)}$ with pressure in CSTR

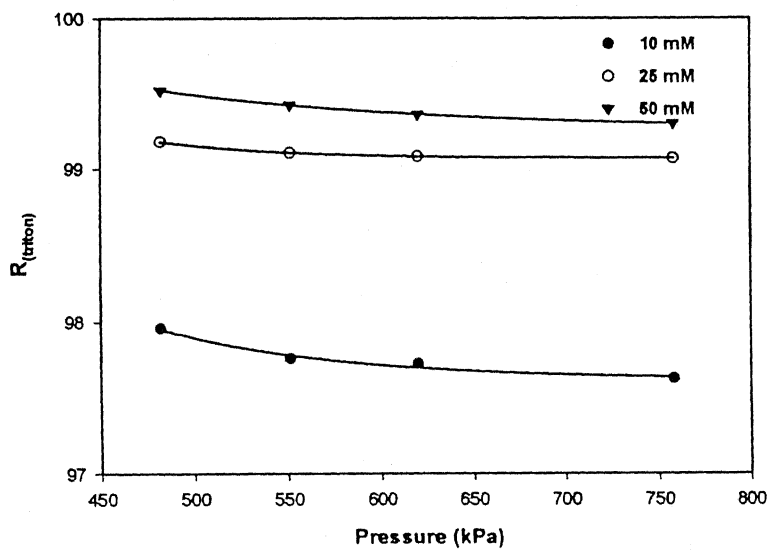


Fig.5.21 Variation of $R_{(triton)}$ with pressure CSTR

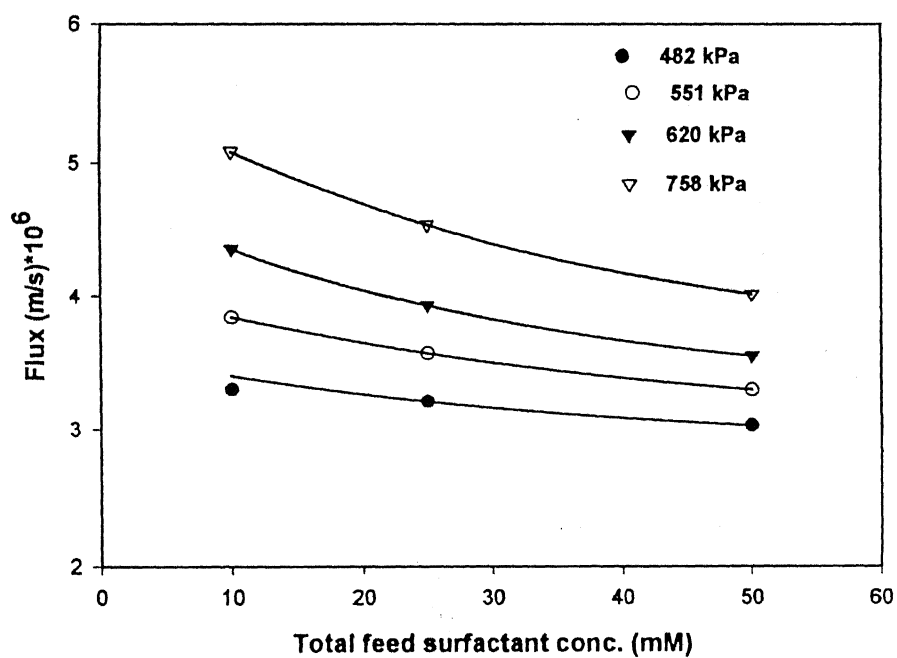


Fig.5.23 Variation of permeate flux with total feed surfactant conc. in CSTR

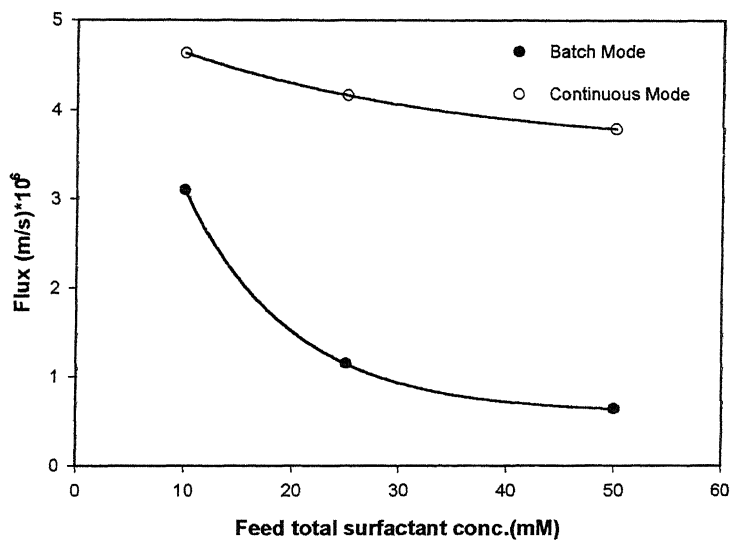


Fig.5.24 Variation of flux with feed total surfactant conc.

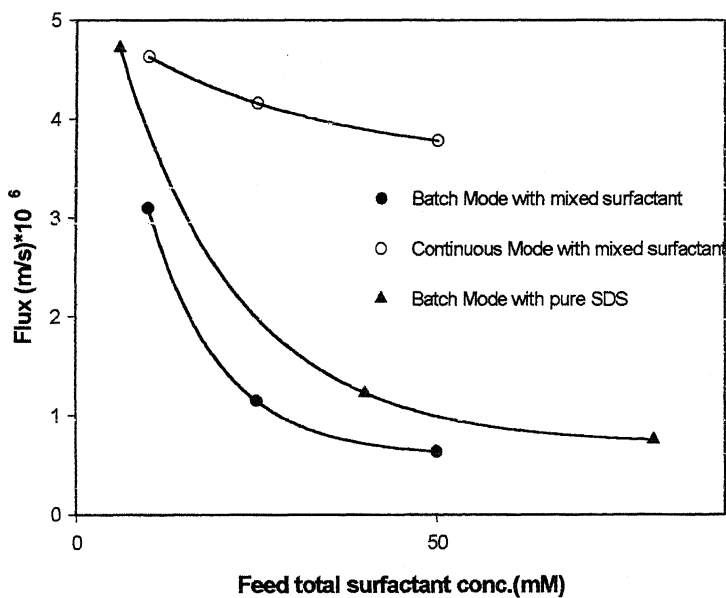


Fig.5.25 Variation of flux with feed total surfactant conc.

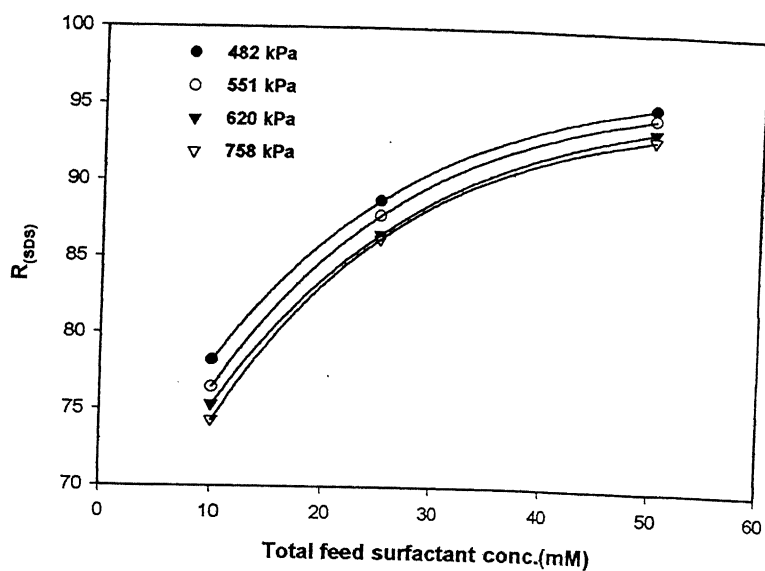


Fig.5.26 Variation of $R_{(SDS)}$ with total feed surfactant conc.in CSTR

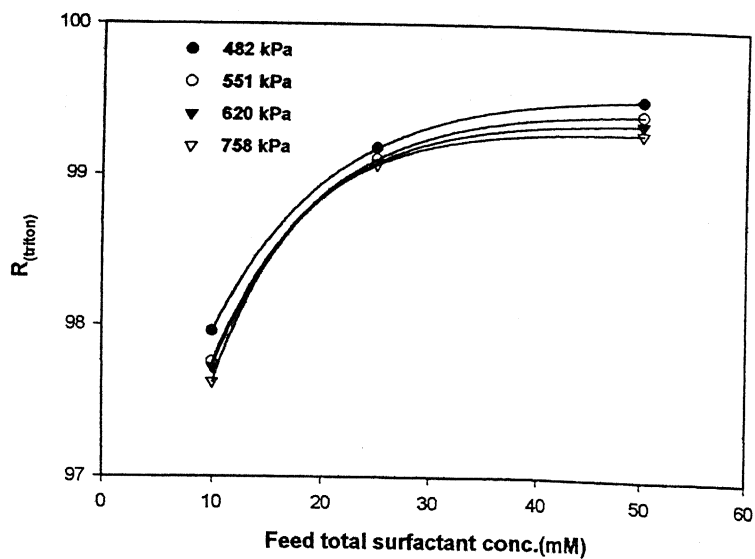


Fig.5.27 Variation of $R_{(triton)}$ with total feed surfactant conc.in CSTR

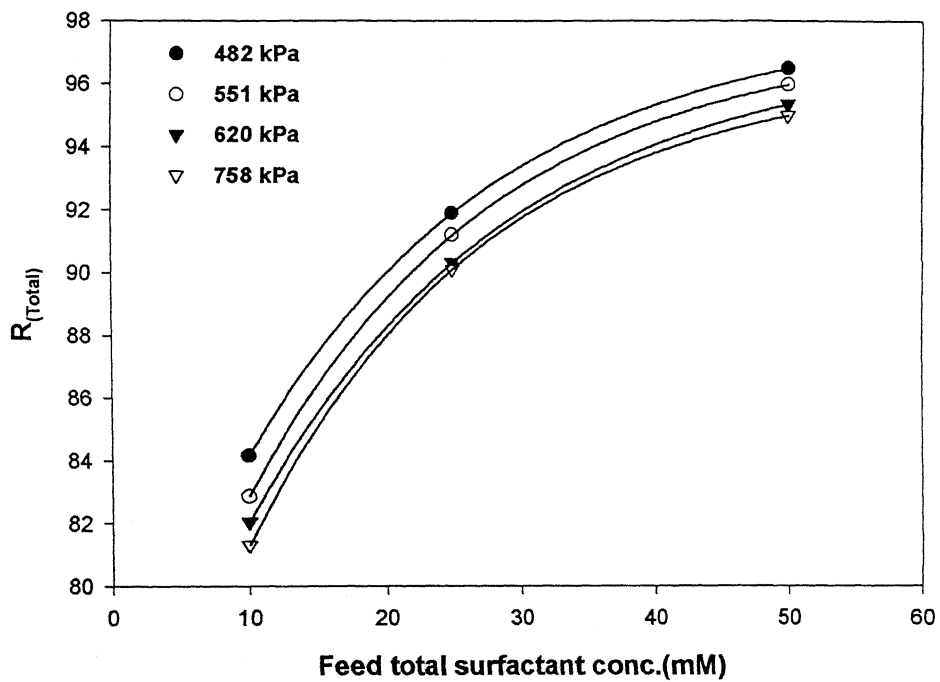


Fig.5.28 Variation of $R_{(Total)}$ with feed total surfactant conc.in CSTR

5.3 Optimization of operating conditions

All the results of CSTR mode MEUF operation to observe influence of total feed concentration and pressure on steady state permeate flux and retentions of surfactant were utilized to optimize the process variables (total feed concentration and pressure). It was therefore necessary to obtain such variations in terms of mathematical equations.

5.3.1 Fitting models for permeate flux and retentions

Following best fit equations were developed for the purpose of optimization of process variables.

Permeate flux

$$J = \frac{6.7623}{\left[1 + \left(\frac{\Delta P - 846.4306}{526.8446}\right)^2\right] \left[1 + \left(\frac{e^{-0.025C} - 2.1856}{2.4738}\right)^2\right]}$$

Retention

$$R_{(Total)} = 114.1378 * \exp \left\{ -0.5 \left[\left(\frac{\Delta P + 3831.2009}{7493.3212} \right)^2 + \left(\frac{C - 47.15}{68.2683} \right)^2 \right] \right\}$$

Where C = Total feed surfactant concentration in mM

ΔP = applied pressure in kPa

Optimization

Above empirical equations were used for data generation of permeate flux and retention of total surfactant for the purpose of optimization of operating conditions like pressure and total feed concentration. As mentioned earlier NSGA-II was employed for optimization. Results of optimization are shown in Fig.5.29 (numerical values are given in Table D1). As per the optimization technique all the points are optimized points and none of them are dominating any other. However, the point (**Total feed concentration: 41.5 mM; and Pressure: 758 kPa** → **Optimized variables**) where sudden decrease of flux occurs with retention of total surfactant was taken as the optimized condition for the present case study, and described in the following section

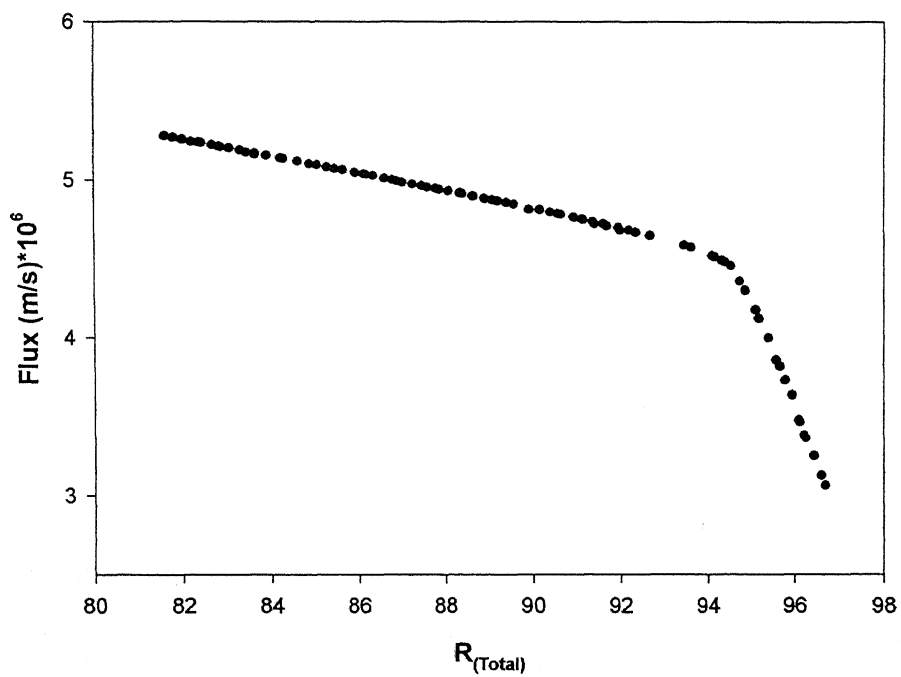


Fig.5.29 Variation of flux with $R_{(Total)}$ under optimized conditions in CSTR

5.4 Case study

The present work, as stated earlier, was carried out with the aim of removing metal ion (present case: Cu^{++} , in the form of copper sulphate), using mixed surfactants, during MEUF operation under optimized conditions of process variables; as the removal characteristics of metal ion depends upon, largely present, retention characteristics of mixed surfactants during MEUF operation; the process variables of which are already optimized with respect to retention characteristics of mixed surfactants.

5.4.1 Ultrafiltration of copper in absence of Surfactant

In order to observe the retention characteristics of aqueous solution of copper ion, it was felt appropriate to conduct batch mode simple UF experiments and observe permeate flux as well as retention, without using surfactants (called blank runs). However, some precautions were taken before conducting experiments. Firstly, membrane was saturated with copper solution in order to minimize Cu^{++} ion adsorption on membrane. This was done by keeping the membrane in copper solution for overnight. Membrane was then placed into UF cell to observe copper ion retention characteristics. Feed concentrations of copper ion were varied from 2 to 4mM. Fig.5.30 shows the variation of flux with time. It was observed that flux continuously decreased till around 160 minutes before attaining a constant value. Since, 5000 MWCO neutral membrane could not have either rejected or retained such a charged and small size ion, the only possibility of flux decline could be due to membrane pore plugging due to adsorption. In fact, this is the reason also for decline of percent retention of copper, as shown in Fig.5.31, with time. More the value of copper feed concentration more will be the decline in flux (Fig.5.30) due to pore plugging through adsorption. However, with increase in copper feed concentration percent retention may fall, particularly during early stages of batch UF (Fig.5.31) as the membrane is neither retaining nor rejecting; it is only losing permeability due to adsorption. In spite of adsorption, maximum of 7 % retention of copper was observed at the highest feed concentration of 4 mM (Fig.5.31). Such a low value of copper retention

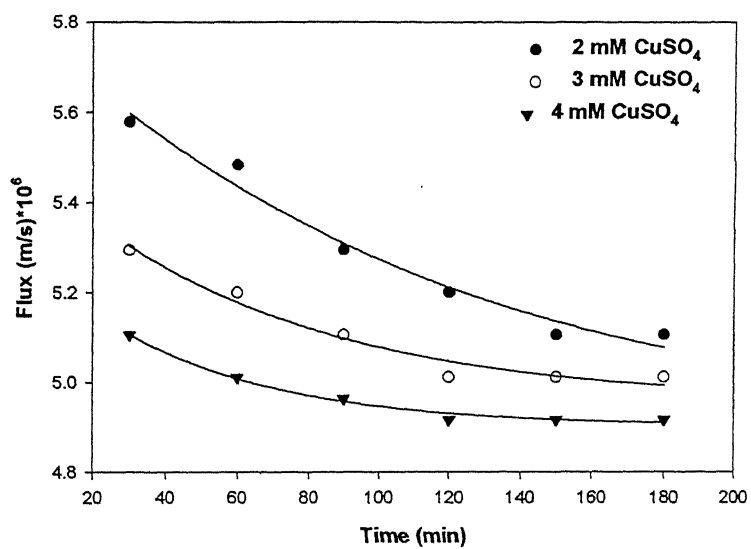


Fig 5.30 Variation of flux with time in batch mode for exclusive runs of copper

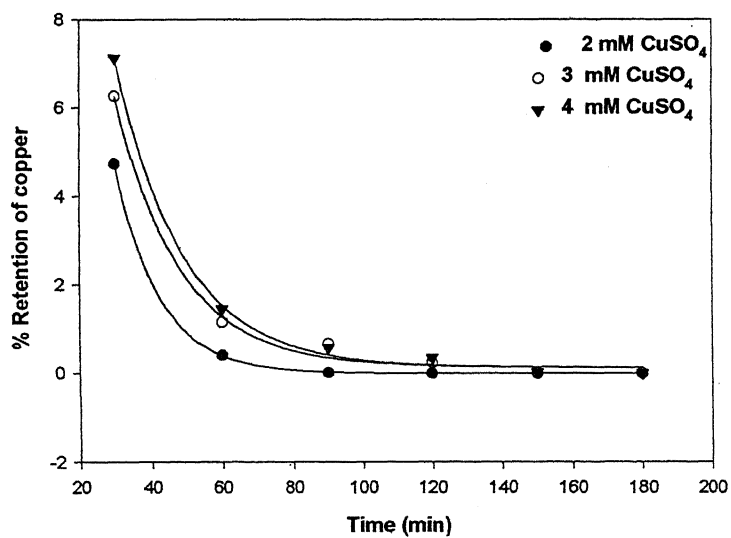


Fig.5.31 Variation of copper retention with time in copper exclusive runs in batch mode

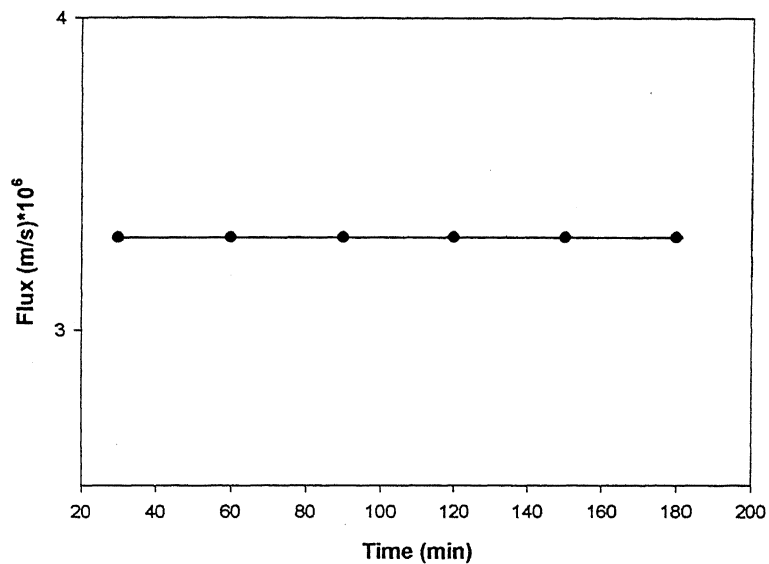


Fig 5.32 Permeate flux vs.time at 758 kPa and 41.5 mM total surfactant conc. for all conc. of CuSO_4 in CSTR

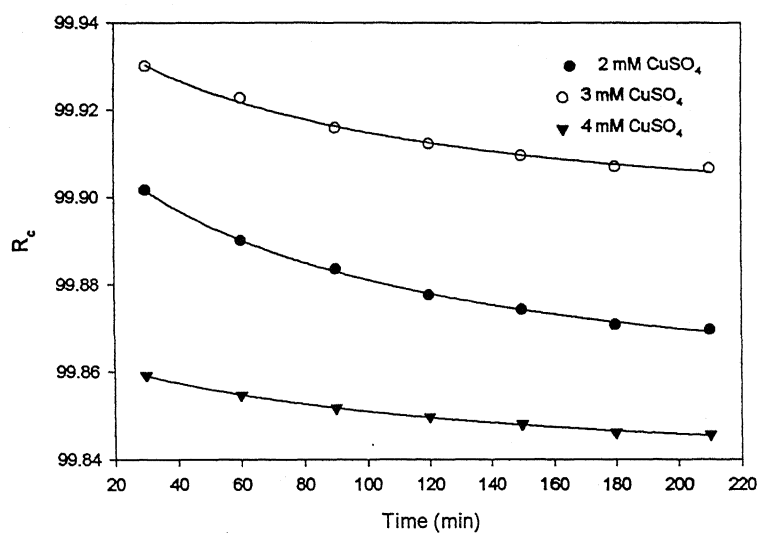


Fig.5.33 Variation of R_e with time at pressure = 758 kPa and total surfactant conc.=41.5 mM in CSTR

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Ultrafiltration experiments were carried out with SDS (anionic) and Triton X-100 (non-ionic) surfactant mixture in 7:3 ratios, respectively, in continuous stirred tank reactor (CSTR) mode (designed and fabricated) and in batch mode UF cells, in order to study retention characteristics of surfactants mixture, using 5000 MWCO neutral membrane. Based on experimental results and obtained optimized process variables following conclusions may be drawn:

1. Permeate flux decreased with time in batch mode (without stirring), indicating significant effect of concentration polarization and presence of micellar aggregation layer. Percent retention of surfactant increased with increase in feed surfactant concentration.
2. In CSTR mode, permeate flux was observed to be independent of time, indicating absence of concentration polarization as well as absence of any build up of resistance layer over membrane surface. Further, percent retentions were high in CSTR mode compared to batch mode. Thus, CSTR mode UF operation was found to be much suitable over batch mode.
3. No significant affect was found on the retention of surfactants with increase in pressure. However, small decrease of retention values with increasing pressure may be because of breakage of micelles.
4. Permeate flux decreased with increase in total surfactants concentration which may due to increase of viscosity (feed side); while, percent retention increased with increase in total feed concentration because of increase in number of micelles in the feed side.
5. Optimization of process variables needed experimental data fitting and accordingly best fit equations were developed to correlate permeate flux and retention against process variables like pressure and total surfactants concentration. Further, optimization was carried out using NSGA-II.
6. Following operating optimized conditions were chosen for successive MEUF studies:

Total feed concentration: 41.5 mM; and Pressure: 758 kPa → Optimized variables

7. Optimized conditions were used for removal of metal ion (present case: copper ion). Very high percent of removals (beyond 99.8) were achieved
8. Thus, with the optimized conditions of SDS and Triton X-100 surfactants mixture, MEUF of copper ion (in the cationic form in aqueous medium) may be carried out for the efficient removal of copper ion as well as surfactants mixture; both being the important feature of the process.

6.2 Recommendations

1. The studies may be extended using different MWCO membrane and different types of membranes.
2. Effect of stirring speed and temperature on the permeate flux and retention of surfactants can be studied.
3. Experiments can be carried out with different ratios of SDS and Triton to study the influence of ratios on the retention characteristics.
4. Theoretical model may be developed and can be used for optimization.

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Appendix A

Table A1 Properties of SDS

Property	Value
Molecular weight	288.38 g/mol
Molecular formula	C ₁₂ H ₂₅ NaOSO ₃
CMC	8 mM
Aggregation number	~100
Density	1 g/ml
Mean micelle size at 10 mM conc.	4.6 nm

Table A2 Properties of Triton X-100

Property	Value
Molecular weight	646.87
Molecular formula	C ₃₄ H ₆₂ O ₁₁
CMC	0.2 mM
Aggregation number	100-134
Density	1.065 g/ml
Mean micelle size at 10 mM conc.	8.5 nm
Viscosity at 25°C	240 cp
Pour point	7°C
Cloud point (1% aqueous solution)	63-69°C

Appendix B

B1 Estimation of Hydraulic Membrane resistance

The hydraulic membrane resistance is given by:

$$R_m = \frac{1}{\mu_w} \left(\frac{\Delta P}{J_w} \right)$$

Using following data given in Table B1, the membrane resistance was found to be $7.888 \times 10^{13} \text{ m}^{-1}$.

ΔP (kPa)	Water Flux $\times 10^6$ (m/s)
344	4.018
482	6.145
620	8.036

Table B1 Water Flux vs. Applied pressure

Appendix C

Experimental Data of UF with surfactants in Batch Mode

SDS Exclusive runs

Time(min)	Permeate Flux*10 ⁶				
	[SDS]=6mM	[SDS]=40mM	[SDS]=80mM	[SDS]=140mM	[SDS]=200mM
15	7.5636	2.4581	1.5127	1.0399	0.8509
30	6.6181	2.0800	1.1345	0.8509	0.6145
45	6.1454	1.8909	1.0400	0.7090	0.4254
60	0.3309	0.6145	0.8981	1.7490	5.7672
90	0.2363	0.4727	0.8509	1.4181	5.1999
120	0.3781	0.7563	0.7563	1.2290	4.7272

Table C1 Permeate Flux vs. Time at different feed SDS conc.

Time(min)	Percent retention of SDS				
	[SDS]=6mM	[SDS]=40mM	[SDS]=80mM	[SDS]=140mM	[SDS]=200mM
15	42.910	79.467	88.580	92.600	95.460
30	39.740	78.450	88.480	90.700	95.38
45	37.410	77.073	85.710	89.970	94.760
60	35.890	75.950	84.465	88.090	93.635
90	34.010	73.468	83.530	85.030	92.000
120	33.350	73.152	80.030	84.720	91.200

Table C2 Percent retention of SDS Flux vs. Time at different feed SDS conc.

[mixed] = mixed surfactant conc. in feed solution

Time(min)	Permeate Flux*10 ⁶		
	[mixed]=10mM	[mixed]=25mM	[mixed]=50mM
15	4.0180	2.2681	1.4177
30	3.7800	1.7551	1.1814
45	3.6230	1.6876	1.0397
60	3.5300	1.5526	0.8979
75	3.3100	1.4176	0.8034
90	3.2200	1.2826	0.7561
105	3.1700	1.2151	0.6616
120	0.6380	1.1475	3.1000

Table C3 Permeate Flux vs. Time at different feed conc. of mixed surfactants

Time(min)	Percent retention of SDS		
	[mixed]=10mM	[mixed]=25mM	[mixed]=50mM
15	56.350	79.060	87.383
30	50.400	70.230	82.890
45	44.660	66.855	79.676
60	41.850	62.210	77.540
75	39.500	60.340	74.780
90	37.273	58.210	73.280
105	36.950	55.914	72.260
120	35.870	54.750	71.710

Table C4 Percent retention of SDS vs. Time at different feed conc. of mixed surfactants

Time(min)	Percent retention of Triton		
	[mixed]=10mM	[mixed]=25mM	[mixed]=50mM
15	83.416	86.300	92.280
30	75.146	79.330	89.870
45	70.605	78.050	87.890
60	67.700	75.600	86.047
75	65.370	73.620	84.166
90	63.070	71.710	82.427
105	60.318	70.224	60.318
120	59.155	69.350	59.155

Table C5 Percent retention of Triton vs. Time at different feed conc. of mixed surfactants

Time(min)	Percent retention of Total surfactant		
	[mixed]=10mM	[mixed]=25mM	[mixed]=50mM
15	64.572	81.240	88.855
30	57.951	70.617	85.029
45	52.230	69.521	82.147
60	49.844	65.560	80.100
75	47.301	62.880	77.606
90	46.120	60.700	76.040
105	44.980	59.45	74.967
120	43.960	58.776	74.082

Table C6 Percent retention of Triton vs. Time at different feed conc. of mixed surfactants

Experimental Data of UF with Mixed surfactants (SDS and Triton X-100 in 7:3 ratio) in CSTR Mode

Time(min)	Permeate Flux*10 ⁶			
	$\Delta P=482\text{kPa}$	$\Delta P=551\text{kPa}$	$\Delta P=620\text{kPa}$	$\Delta P=758\text{kPa}$
30	3.4980	4.0654	4.6327	5.3890
90	3.4980	4.0654	4.6327	5.3890
150	3.4980	4.0654	4.6327	5.3890
180	3.4980	4.0654	4.6327	5.3890

Table C7 Permeate Flux vs. Time at different pressure at total feed conc. of 10 mM

Time(min)	Permeate Flux*10 ⁶			
	$\Delta P=482\text{kPa}$	$\Delta P=551\text{kPa}$	$\Delta P=620\text{kPa}$	$\Delta P=758\text{kPa}$
30	3.4000	4.1600	3.7818	4.8220
90	3.4000	4.1600	3.7818	4.8220
150	3.4000	4.1600	3.7818	4.8220
180	3.4000	4.1600	3.7818	4.8220

Table C8 Permeate Flux vs. Time at different pressure at total feed conc. of 25 mM

Time(min)	Permeate Flux*10 ⁶			
	$\Delta P=482\text{kPa}$	$\Delta P=551\text{kPa}$	$\Delta P=620\text{kPa}$	$\Delta P=758\text{kPa}$
30	3.2145	3.4981	3.7817	4.2540
90	3.2145	3.4981	3.7817	4.2540
150	3.2145	3.4981	3.7817	4.2540
180	3.2145	3.4981	3.7817	4.2540

Table C9 Permeate Flux vs. Time at different pressure at total feed conc. of 50 mM

Time(min)	Percent retention of SDS			
	$\Delta P = 482 \text{ kPa}$	$\Delta P = 551 \text{ kPa}$	$\Delta P = 620 \text{ kPa}$	$\Delta P = 758 \text{ kPa}$
30	80.670	78.618	76.920	75.789
60	79.600	77.578	76.056	75.269
90	78.775	77.075	75.628	74.902
120	78.974	77.550	75.327	74.543
150	78.250	76.485	75.332	74.317

Table C10 Percent retention of SDS vs. Time at different pressure at total feed conc. of 10 mM

Time(min)	Percent retention of Triton			
	$\Delta P = 482 \text{ kPa}$	$\Delta P = 551 \text{ kPa}$	$\Delta P = 620 \text{ kPa}$	$\Delta P = 758 \text{ kPa}$
30	98.446	98.182	97.964	97.873
60	98.185	97.984	97.839	97.782
90	98.069	97.872	97.760	97.705
120	97.966	97.790	97.721	97.656
150	97.960	97.757	97.724	97.624

Table C11 Percent retention of Triton vs. Time at different pressure at total feed conc. of 10 ml

Time(min)	Percent retention of total surfactants			
	$\Delta P = 482 \text{ kPa}$	$\Delta P = 551 \text{ kPa}$	$\Delta P = 620 \text{ kPa}$	$\Delta P = 758 \text{ kPa}$
30	86.010	84.496	83.284	82.661
60	85.182	83.709	82.898	81.981
90	84.571	83.324	82.566	81.7693
120	84.373	83.294	82.344	81.593
150	84.175	83.023	82.238	81.475

Table C12 Percent retention of total surfactants vs. Time at different pressure at total feed conc. of 10 mM

Time(min)	Percent retention of SDS			
	$\Delta P = 482 \text{ kPa}$	$\Delta P = 551 \text{ kPa}$	$\Delta P = 620 \text{ kPa}$	$\Delta P = 758 \text{ kPa}$
30	90.338	89.358	88.303	87.947
60	89.500	88.853	87.673	87.435
90	89.100	88.128	87.034	86.724
120	88.594	88.257	86.946	86.484
150	88.764	87.797	86.544	86.255

Table C13 Percent retention of SDS vs. Time at different pressure at total feed conc. of 25 mM

Time(min)	Percent retention of Triton			
	$\Delta P = 482 \text{ kPa}$	$\Delta P = 551 \text{ kPa}$	$\Delta P = 620 \text{ kPa}$	$\Delta P = 758 \text{ kPa}$
30	99.260	99.210	99.172	99.150
60	99.215	99.162	99.117	99.110
90	99.194	99.126	99.093	99.085
120	99.183	99.114	99.085	99.073
150	99.180	99.010	99.082	99.069

Table C14 Percent retention of Triton vs. Time at different pressure at total feed conc. of 25 mM

Time(min)	Percent retention of total surfactants			
	$\Delta P = 482 \text{ kPa}$	$\Delta P = 551 \text{ kPa}$	$\Delta P = 620 \text{ kPa}$	$\Delta P = 758 \text{ kPa}$
30	93.301	92.289	91.563	91.309
60	92.416	91.768	91.106	90.841
90	92.129	91.594	90.624	90.243
120	91.773	91.549	90.588	90.238
150	91.891	91.370	90.502	90.0962

Table C15 Percent retention of total surfactants vs. Time at different pressure at total feed conc. of 10 mM

Time(min)	Percent retention of SDS			
	$\Delta P=482\text{kPa}$	$\Delta P=551\text{kPa}$	$\Delta P=620\text{kPa}$	$\Delta P=758\text{kPa}$
30	95.997	95.141	94.41	94.053
60	95.682	94.895	94.078	93.724
90	95.462	94.701	93.848	93.465
120	95.270	94.541	93.700	93.0197
150	95.206	94.498	93.631	93.167

Table C16 Percent retention of SDS vs. Time at different pressure at total feed conc. of 50 mM

Time(min)	Percent retention of Triton			
	$\Delta P=482\text{kPa}$	$\Delta P=551\text{kPa}$	$\Delta P=620\text{kPa}$	$\Delta P=758\text{kPa}$
30	9.062	99.525	99.451	99.379
60	99.557	99.480	99.411	99.332
90	99.543	99.430	99.831	99.315
120	99.535	99.430	99.367	99.305
150	99.525	99.428	99.365	99.304

Table C17 Percent retention of Triton vs. Time at different pressure at total feed conc. of 50 mM

Time(min)	Percent retention of total surfactants			
	$\Delta P=482\text{kPa}$	$\Delta P=551\text{kPa}$	$\Delta P=620\text{kPa}$	$\Delta P=758\text{kPa}$
30	97.078	96.470	95.922	95.647
60	96.844	96.271	95.679	95.407
90	96.686	96.120	95.510	95.221
120	96.55	96.008	95.490	95.030
150	96.502	95.977	95.352	94.989

Table C18 Percent retention of total surfactants vs. Time at different pressure at total feed conc. of 50 mM

Appendix D

Optimization Results

S.No.	Flux(m/s)*10 ⁶	R _(Total)	Feed total surfactant. Conc.(mM)	Pressure (psi)
1	5.0378	86.12509	17.54029	109.9788
2	5.21313	82.83571	11.93741	109.9386
3	3.85982	95.5827	44.14478	89.97381
4	4.97353	87.25963	19.66508	109.8507
5	5.15665	83.90938	13.68805	109.9738
6	4.92942	88.09002	21.32997	109.9389
7	4.68316	92.01197	30.89544	109.2605
8	3.38139	96.23213	44.17713	77.49944
9	4.81367	89.92567	25.2971	109.3451
10	4.9523	87.58898	20.29588	109.6909
11	4.30071	94.88382	47.13016	105.0014
12	5.25915	81.99001	10.60806	109.9891
13	3.732	95.77966	44.63016	86.72498
14	4.36091	94.75102	47.1326	107.5014
15	4.7498	91.16961	28.53884	109.9392
16	4.8726	89.10841	23.4984	109.9643
17	5.0459	85.92797	17.17057	109.8507
18	4.81033	90.17186	25.96101	109.9344
19	4.81122	90.16917	25.95934	109.9737
20	4.98527	87.02086	19.19801	109.7836
21	4.75158	91.14111	28.46071	109.9392
22	4.70904	91.70834	30.02321	109.5833
23	4.3027	94.87967	47.13016	105.0795
24	3.47881	96.09849	44.08573	79.97746
25	4.85572	89.4054	24.16414	109.9709
26	4.97554	87.25076	19.65531	109.9289
27	3.63628	95.93467	47.13016	85.00131
28	4.84553	89.58358	24.572	109.9758
29	4.51481	94.15574	40.30952	109.7823
30	3.63809	95.93436	46.97513	85.00135
31	5.16347	83.64642	13.22678	109.6262
32	5.16773	83.63774	13.22663	109.8084
33	4.98389	88.9119	23.06795	109.9704
34	5.17698	83.45445	12.92465	109.7836
35	3.25422	96.4519	46.97635	75.00134
36	3.73201	95.77959	44.62894	86.72498
37	4.72191	91.4283	29.16979	109.306

38	4.96432	87.47099	20.09034	109.9737
39	4.86572	89.22043	23.74437	109.9386
40	5.02647	86.33429	17.92466	109.9789
41	4.58801	93.44372	36.34036	109.9155
42	3.46588	96.11908	44.15882	79.6674
43	5.11904	84.61541	14.87671	109.9805
44	5.25789	82.00777	10.63461	109.974
45	5.20798	82.86775	11.97632	109.7735
46	4.17951	95.11546	47.13016	100.6263
47	4.78609	90.57881	26.97633	109.9389
48	3.82181	95.67534	47.1326	89.97388
49	5.13794	84.2281	14.21376	109.8914
50	4.52168	94.11668	40.09036	109.9386
51	4.79674	90.41693	26.57365	109.9892
52	5.03567	86.16438	17.61216	109.9788
53	5.06385	85.64305	16.66978	109.9803
54	5.27891	81.61253	10.02319	109.9752
55	4.4828	94.4012	42.52322	109.9949
56	5.10213	84.88208	15.32364	109.8507
57	4.57442	93.60764	37.13992	109.9744
58	4.73568	91.39319	29.16254	109.9384
59	4.64863	92.68301	33.26342	109.9543
60	4.89816	88.65937	22.52366	109.9705
61	5.20167	83.06525	12.30835	109.9752
62	4.85589	89.405	24.16414	109.9788
63	4.76466	90.94042	27.9236	109.974
64	4.72142	91.63225	29.86193	109.9997
65	3.25442	96.45182	46.95728	75.00134
66	5.22245	82.67487	11.68381	109.9752
67	3.06304	96.70895	47.13855	70.0013
68	5.11904	84.61541	14.87671	109.9805
69	3.12984	96.62032	46.92508	71.72005
70	4.49235	94.3247	41.66545	109.7823
71	4.99301	86.87885	18.92701	109.7836
72	4.94126	87.87644	20.89543	109.9386
73	5.09545	85.05544	15.63462	109.9803
74	4.9127	88.40049	21.97633	109.9705
75	4.76375	90.95506	27.96266	109.974
76	5.07271	85.46012	16.34034	109.9307
77	5.23605	82.41912	11.27899	109.9752
78	5.26944	81.79088	10.29823	109.9752
79	4.12229	95.18914	44.14432	97.47992
80	4.94691	87.78545	20.71534	109.9705
81	5.13457	84.29131	14.32007	109.8914
82	4.69839	91.97504	30.89544	109.9734
83	5.00091	86.79015	18.7732	109.9389
84	4.91522	88.35648	21.88462	109.9737
85	4.4563	94.53007	44.15409	109.9409
86	4.68206	92.21349	31.65407	109.9643
87	5.00905	86.60858	18.42324	109.8507

88	3.36821	96.25079	44.20215	77.1674
89	4.58801	93.44372	36.34036	109.9155
90	5.23924	82.36454	11.19404	109.9891
91	5.04876	85.92182	17.17057	109.9777
92	4.66895	92.37487	32.16967	109.853
93	5.08039	85.2874	16.02906	109.8507
94	4.78228	90.65363	27.17325	109.9788
95	5.18958	83.2977	12.68524	109.9892
96	3.99981	95.41145	47.12558	95.00868
97	4.89893	88.64565	22.49437	109.9705
98	4.88146	88.94409	23.13463	109.9386
99	5.24308	82.2058	10.92896	109.7699
100	4.92942	88.09002	21.32997	109.9389

Table D1 Permeate flux vs. Retention of total surfactants under optimized conditions

Appendix E

Case study

Copper exclusive runs in Batch Mode

Time(min)	Permeate Flux*10 ⁶		
	[Copper]=2mM	[Copper]=3mM	[Copper]=4mM
30	5.5781	5.2945	5.1054
60	5.4836	5.2000	5.0109
90	5.2945	5.1054	4.9636
120	5.2000	5.0109	4.9163
150	5.1054	5.0109	4.9163
180	5.1054	5.0109	4.9163

Table E1 Permeate Flux vs. Time for exclusive runs of copper in batch mode at 758 kPa Pressure

Time(min)	Retention of copper		
	[Copper]=2mM	[Copper]=3mM	[Copper]=4mM
30	4.734	6.261	7.127
60	0.4008	1.160	1.456
90	.0123	0.657	0.578
120	0	0.235	0.346
150	0	0.013	0.018
180	0	0	0

Table E2 Retention of copper vs. Time for exclusive runs of copper in batch mode at 758 kPa Pressure

Time(min)	Permeate Flux*10 ⁶		
	[Copper]=2mM	[Copper]=3mM	[Copper]=4mM
30	3.2983	3.2983	3.2983
60	3.2983	3.2983	3.2983
90	3.2983	3.2983	3.2983
120	3.2983	3.2983	3.2983
150	3.2983	3.2983	3.2983
180	3.2983	3.2983	3.2983

Table E3 Permeate Flux vs. Time in CSTR under optimized conditions with copper

Time(min)	Retention of copper		
	[Copper]=2mM	[Copper]=3mM	[Copper]=4mM
30	99.901	99.930	99.85923
60	99.890	99.922	99.854
90	99.883	99.916	99.852
120	99.877	99.912	99.850
150	99.874	99.909	99.848
180	99.870	99.907	99.846
210	99.869	99.906	99.845

Table E4 Retention of copper vs. Time in CSTR under optimized conditions with copper